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OPTIMAL CHELANT/COPPER RATIOS FOR MAXIMIZING COPPER SOLUBILITY IN NATURAL WATER USING CITRIC ACID AND TRIETHANOLAMINE

ILENR/RE-EH-86/09

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Illinois Department of
Energy and Natural Resources

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CONTENTS

Page

Introduction 1
Acknowledgments 7

Objectives and Scope 8

Materials and Methods 9

Results and Discussion 12
Optimal copper/chelant ratio 12
Particulate adsorption 15
Cutrine study 16
Regression analysis 17

Summary 18

Tables and Figures 20

References 40

Appendix 43

OPTIMAL CHELANT/COPPER RATIOS
FOR MAXIMIZING COPPER SOLUBILITY IN NATURAL WATERS
USING CITRIC ACID AND TRIETHANOLAMINE

by Raman K. Raman and Billy K. Cook

INTRODUCTION

Taste and odor problems that plague waterworks using impoundments as a source can most often be attributed to algal blooms, mainly blue-greens (Sigworth, 1957). These taste and odor problems are compounded by other problems such as reduced filter runs, increased chemical costs, etc. Physical solutions to the problems such as harvesting of algae or control of excessive nutrient inputs can be extremely costly and time consuming in comparison to chemical methods of bloom control. Although several types of algicides are commercially available, copper formulations seem to enjoy the greatest popularity due in part to their relatively low toxicity to higher organisms, particularly fish, when applied at accepted algicidal levels (Mackenthun and Cooley, 1952).

The relatively low toxicity of copper to humans is reflected in finished water quality standards, which set the maximum allowable concentrations of copper at 5.0 mg/liter (Pollution Control Board, 1982). According to Water Quality and Treatment (1950), copper may be beneficial or even essential

for the growth of living organisms. The USEPA has proposed an RMCL (i.e., Recommended Maximum Contaminant Level) for copper of 1.3 mg/L in drinking water. The average daily human intake of copper from water and foodstuffs is generally about 2-5 mg. Richey and Roseboom (1978) have also demonstrated that the 14-day TL-50 (i.e., the concentration at which a 50% mortality occurs within 14 days in an acute toxicity flow-through test) for bluegill and channel catfish, native to Illinois, is an order of magnitude higher than accepted algicidal levels.

The toxicity of copper to nuisance phytoplankton populations in recreational and water supply lakes has been an accepted fact since the turn of the century (Moore and Kellerman, 1904). Copper sulfate pentahydrate has been the most widely used algicide in the United States, with yearly applications approaching 20 million pounds (Fitzgerald, 1971). However, alkaline, hard waters, such as those found in central and northern Illinois lakes, are known to require greater copper sulfate "loading" for effective algicidal action (Mackenthun, 1969; Fitzgerald, 1971) due to rapid conversion of copper to possibly non-toxic forms by hydrolysis, complexation, adsorption, and precipitation reactions with inorganic species common to fresh waters (Sylva, 1976). This is particularly true in central Illinois where alkalinity and hardness are high, with pH's in the range of 7.5 to 8.5 (Stiff, 1971a).

Figure 1 (from Sylva, 1976) shows the speciation of copper in typical fresh waters as a function of pH. The most rapid changes in copper chemistry occur in the pH range 6.5 - 8 such

that less than 10% of the copper present at pH 8 is in the form of cupric ions. Hydrolysis and precipitation products dominate the chemistry of copper at this pH.

Stable complexes of copper with organics typical of fresh waters, such as humic and fulvic acids produced by decaying vegetation, also tend to reduce the concentration of available copper (Shuman and Woodward, 1977; McKnight, 1981; Sylva, 1976). Likewise, Gachter and others (1978) point to the possibility that complexation by macromolecular organic material in lake water may be ecologically significant in regulating the availability of copper to aquatic organisms.

Adsorption of copper onto suspended solids is considerable above pH 6.5 (James and Healy, 1972) and plays a significant role in the reduction of total dissolved copper (TDCu). Studies by Wagemann and Barica (1979) indicated that the rate of disappearance of copper was always slower in filtered than in unfiltered samples. Results by Stiff (1971b) also point to the presence of suspended solids having a profound effect on the physical state of copper in aquatic environments.

These mechanisms of copper "loss" make it difficult at best to maintain a 0.1 to 0.3 mg/L concentration of dissolved copper necessary for algicidal action (Mackenthun, 1969; Muchmore, 1978). But in order to do so, applicators have simply increased frequency and dosages in order to "overpower" the effects of precipitation, complexation, and adsorption. Currently, no specific guidelines exist for the amount or

frequency of chemical application to water supply impoundments. For waters with alkalinity greater than 40 mg/L, Mackenthun (1969) advocates the application of copper sulfate at a rate of 1 mg/L as $CuSO_4 \cdot 5H_2O$ (0.25 mg/L as Cu^{+2}) for the upper 2 feet of water regardless of the actual depth of impoundments. On an acreage basis, this concentration amounts to 5.4 lbs/surface acre. For waters with alkalinities less than 40 mg/L, Mackenthun recommends application rates of 0.3 mg/L as copper sulfate pentahydrate. Fair et al. (1971) recommend raising copper sulfate dosages by as much as 5% for each 10 mg/L of alkalinity as $CaCO_3$. In addition, even larger dosages may be indicated as algae shift to more resistant species (Hanson and Stefan, 1984).

This increase in application rates not only increases the cost of maintaining water quality in an impoundment, but also intensifies long-term effects associated with elevated copper dosages, such as in the Fairmont Lakes, Minnesota (Hanson and Stefan, 1984). These effects may include a) copper accumulation in sediments, b) tolerance adjustments of certain species of algae, c) shift of species from green to blue-green algae and from game fish to rough fish, d) disappearance of macrophytes, and e) reduction in benthic macroinvertebrates (Gibson, 1972; Iskander and Keeney, 1974). These cumulative side effects point to the need to reduce dosage requirements by enhancing the solubility of copper in a natural system.

Although the use of chelating agents, such as citric acid monohydrate (Kothandaraman et al., 1980; Stern et al., 1978)

and triethanolamine, or TEA (Applied Biochemists, Inc., 1976) has been demonstrated to enhance copper solubility in surface water impoundments (Illinois Natural History Survey, 1975; Gelfand, 1946), copper sulfate continues to be used alone in most cases. This is puzzling in light of the fact that when algal blooms form, the pH is typically about 8.0, in which case the precipitation and complexation of the copper is imminent.

The continued use of copper sulfate alone is due partly to the lack of published research outlining desirable chelants and optimum copper/chelant ratios, but mainly to the non-uniform speciation in U.S. surface waters. The latter has made it extremely difficult to empirically determine the optimal, i.e., most cost effective, copper/chelant ratios to maintain an algicidal copper concentration. Given the advantage of premixing and elevated levels of chelants, commercial copper formulations, e.g., Cutrine, AV-70, etc., can ensure initially high concentrations of the complex, which may or may not be stable in the treated lake as outlined in disclaimers which accompany these algicides. Non-uniform speciation makes some products more effective than others in different regions of the country depending on the stability of the complex vs. competition for the copper.

Sylva (1976) indicates that at pH 8 a prospective ligand would need an effective formation constant on the order of 10^5 to effectively bind free copper ions in a natural system. This is by no means a hard-and-fast rule, as competition effects for free copper ions can vary greatly from system to system, but it

does place some doubt on the efficacy of citric acid monohydrate and triethanolamine as chelating agents considering their relatively small stability constants (Sillen and Martell, 1964).

Another important aspect of copper chelation is the issue of whether chelated forms of copper or soluble copper salts retain their algicidal effect. McKnight (1981) maintains that the toxicity of copper is determined by cupric ion activity and not by the total copper concentration. Wagemann and Barica (1979) introduced their "total toxic copper" concept, which, in the absence of chelating agents, included Cu^{+2}, $Cu(OH)_2$, and $CuOH^+$. From Elder and Horne (1978):

> Complexation of copper is generally assumed to reduce the availability of the metal for biological uptake, although not necessarily by removing it from solution (Horne and Goldman, 1974). On the other hand, Gachter and others (1974) and Sylva (1976) correctly pointed out that this assumption has not been experimentally verified and it is entirely possible that some or all natural copper complexes are actually available.

Some studies have indicated that precipitated copper salts and copper-citric acid complexes are no less effective as toxic agents even when tested with different algae in which required concentrations for toxicity varied from 0.5 to 1.0 mg copper sulfate/L (Fitzgerald, 1963). It should be noted that the study conducted by Fitzgerald (1963) indicated that the toxicity of copper to bluntnose minnow and several sunfishes was reduced in

the presence of citric acid without its algicidal properties being affected. Stern and others (1978), along with Guy and Kean (1979), have similarly verified that citric acid has no adverse effects on the algicidal properties of copper sulfate.

On the other hand, strong chelants such as NTA or EDTA are known to partially or completely counteract copper toxicity (Horne and Goldman, 1974; Gachter, 1978). This would indicate that a delicate balance must be sought between the ability of an added ligand to inhibit precipitation and its interference in biological uptake. Citric acid appears to lie on the razor's edge.

Virtually no information is available on the toxicity of copper-triethanolamine complexes to blue-green algae even though several formulations are currently on the market. In light of its success in the field one would assume its efficacy as an algicide. However, the Illinois Pollution Control Board (Environmental Register, November 7, 1985) found that copper/triethanolamine complexes were not suitable as public water supply algicides because of the possibility of adverse health effects relating to mutagenicity and carcinogenicity. Citric acid, on the other hand, presents no such problem with human consumption as outlined in the Federal Food and Drug Administration's Food Chemical Codex.

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OBJECTIVES AND SCOPE

This study is concerned primarily with enhancement of total dissolved copper (TDCu) by chelation rather than with the algicidal effectiveness of the various forms of copper. If precipitation of the copper by inorganic anions can be inhibited by the presence of a chelating agent such as citric acid monohydrate or triethanolamine, it follows that dosages necessary to maintain algicidal action can be minimized. This would not only reduce the ecological impact of long-term copper sulfate applications but would also result in an enormous reduction in water treatment costs incurred by municipalities using surface impoundments as drinking water sources.

The work itself involved the correlation of percent copper

loss with hardness, alkalinity, pH, and suspended solids along with the determination of minimum chelant/copper ratios necessary to maximize copper solubility. Included in this report is a comparison of the relative stability of copper-citric acid vs. copper-triethanolamine complexes. Thus, guidelines were established for the relative concentrations of chelant and copper necessary for maximum copper solubility under given water quality conditions.

MATERIALS AND METHODS

For the laboratory evaluation it was necessary to choose lakes with typically high alkalinity and hardness in order to accurately simulate real lake conditions. Lake Canton (230 acres) and Lake Eureka (37 acres) both exhibit alkalinities in the range of 160 to 230 mg/L as $CaCO_3$ with a pH range of 7.4 to 8.4, providing ample precipitation and complexation reactions for the purposes of this experiment. To provide comparison, Rend Lake (Benson, Illinois, 18,900 acres) with alkalinities of 40-75 mg/L as $CaCO_3$ was chosen as a relatively soft, low alkalinity lake.

Both Lake Eureka and Lake Canton have had occasion to treat algal blooms with copper sulfate in the past. However, with the installation in recent years of destratification/aeration systems in both lakes, these treatments have been minimized.

Bulk samples (approximately 60 liters) were obtained from

the top 2 feet of the lakes at their deepest points (figure 2). Table 1 contains the background analysis of each bulk lake sample including total and soluble metals, hardness, alkalinity, pH, suspended solids, chloride, sulfate, and conductivity. All analyses were performed as per Standard Methods (APHA, 1980).

Bulk samples from each lake were divided into 250-mL subsamples which were initially dosed with sufficient copper sulfate to provide a theoretical copper concentration of 0.1 mg/L as Cu^{+2}. A chelating agent (for example, citric acid monohydrate) was premixed with the copper sulfate spikes in incremental amounts providing weight/weight ratios of copper sulfate pentahydrate/chelant from 1:0 to 1:9. These premixed spikes were allowed to stand 15 minutes. In addition, a distilled water blank was also dosed with copper to provide a recovery comparison. Following addition of the copper/chelant premix, samples were well mixed and allowed to equilibrate for 2 hours. Next, 50-ml portions of each subsample were filtered (0.45 µm), acidified (1 ml 1+1 HNO_3), and analyzed for soluble copper by flame atomic absorption as per Standard Methods (APHA, 1980). The subsamples were agitated by means of an Eberbach shaker table for 24 hours to inhibit settling, and the analysis was repeated.

Each and every copper/chelant ratio experiment was run in triplicate to ensure accuracy and precision. These tests were repeated with copper sulfate pentahydrate dosages sufficient to provide theoretical copper concentrations of 0.2 and 0.3 mg/L

as Cu^{+2}. All of the above procedures were repeated with triethanolamine (TEA) as the chelating agent.

Spring bulk samples were collected from Lake Canton, Lake Eureka, and Rend Lake on April 12, May 3, and June 7, 1985, respectively. Also, summer samples were collected from these three lakes on June 28, September 10, and August 14, 1985, respectively.

A follow-up study involving the use of Cutrine, a commercially available copper/triethanolamine algicide, required an additional sampling of Lake Eureka on December 13. The pH, alkalinity, and hardness of this sampling were 8.02, 181 mg/L, and 228 mg/L, respectively, and these values are not included in the water quality data table for bulk samples. In this study, 250-ml subsamples from Lake Eureka were spiked with sufficient Cutrine to provide theoretical copper concentrations of 0.2, 0.5, and 0.8 mg/L as Cu^{+2} (dosage requirements listed by Applied Biochemists, the manufacturer, range from 0.4 mg/L to 1.0 mg/L as Cu^{+2}). Identical volumes of distilled water, spiked at the same concentrations, served as the control.

As in previous experiments, each copper concentration was run in triplicate to ensure precision. Cutrine-spiked subsamples were then well mixed and allowed to equilibrate for 2 hours. Next, 50-ml aliquots of each subsample were filtered (0.45 µm), acidified (1 ml 1 + 1 HNO_3) and analyzed for copper by flame atomic absorption as per Standard Methods (APHA, 1980). This analysis was repeated at 24, 48, and 96 hours to

provide a look at the viability of the copper/triethanolamine complex when extended equilibration time for the complex is allowed.

In order to monitor copper loss over an extended period, an experiment involving one Lake Eureka sample (collected on March 18) containing a 0.25-mg/L Cu^{+2} spike and another containing the copper with sufficient citric acid monohydrate to provide a 1:1.25 (w/w) ratio (as $CuSO_4 \cdot 5H_2O/C_6H_8O_7 \cdot H_2O$) was extended to include 48-hour and 96-hour TDCu analyses. In addition, this sample was split, with a portion filtered prior to spiking in order to look at the role played by suspended solids in the loss of soluble copper.

Average results of each copper analysis can be seen in the appendix.

RESULTS AND DISCUSSION

Optimal Copper/Chelant Ratio

Background water quality data for Lake Eureka, Lake Canton, and Rend Lake including pH, alkalinity, hardness, chloride, suspended solids, conductivity, and total and soluble metals can be seen in table 1. Figures 3a-3f indicate the dissolved copper concentration in the aforementioned lake subsamples with copper/chelant ratios of 1:0 to 1:9 for both citric acid and triethanolamine for three different initial

copper concentrations and two different contact periods. Each plot indicates dissolved copper concentrations after a 2-hour equilibration period and again after 24 hours of constant mixing. Spring and summer runs for each of the lakes are illustrated separately.

Individually, these experiments do not reveal a clear "plateau" where additional chelant has no added enhancement effect. However, if the data from all the lake experiments are combined in terms of percent copper remaining in solution vs. copper/chelant ratio, a plateau does emerge for the higher copper concentrations. Figures 4a-4d indicate the average percent copper remaining in solution for all the lakes versus the copper/chelant ratio (w/w) when spiked at the 0.3-mg Cu/L concentration. These plots indicate that enhancement of the copper solubility begins to level off near a 1:5 (w/w) ratio of $CuSO_4 \cdot 5H_2O$:chelant. This appears to be the case for both citric acid and triethanolamine.

A close examination of these plots indicates that although citric acid has an initial tenacity, maintaining higher levels of soluble copper than did the TEA for the first 2 hours, the rate of copper loss over 24 hours is less for the TEA samples, resulting in comparable copper concentrations for both chelants after 24 hours. Since stability constants for these two chelating agents are relatively similar, this could be due to the fact that citric acid is not stable in aqueous solution at very low concentrations and begins to degrade (Merck Index of Chemicals and Drugs). Triethanolamine, on the other hand, is

more stable over extended periods and low concentrations.

It is clear from figures 5a-5d and 6a-6d that this enhancement effect decreases as expected when initial copper concentrations are decreased. Figures 6a-6d show that at copper concentrations on the order of 0.1 mg Cu/L, no clear plateau exists, indicating that at or near these concentrations of copper and chelating agent, there is little or no contribution to the total dissolved copper by these complexes.

Even though application rates and frequency may vary from lake to lake, dissolved copper concentrations in treated lakes should remain in the range of 0.1 to 0.3 mg/L as biologically available copper for required algicidal effects. Figures 7a-7d indicate the average percent copper remaining in solution for all three copper spike concentrations. These averages include all three lakes and both the spring and summer runs. The resulting plots show a definite enhancement effect for both the citric acid monohydrate and triethanolamine, but the plateau is not nearly as well defined as in those representing higher concentrations. Still, it can be seen that for the first few hours, a copper sulfate pentahydrate to chelant ratio (weight/weight) of at least 1:5 provides the maximum effect for the higher concentrations, with the necessary ratio increasing as initial copper concentration decreases.

It should be noted here that Stern et al. (1978), in their study of the algicidal effects of copper sulfate alone and mixtures of copper sulfate-citric acid, used a

weight/weight ratio of 1:8 at a copper sulfate concentration equivalent to 0.5 mg/L as Cu^{+2}. Their study indicated that the addition of citric acid increased the toxicity of copper to *Microcystis*, with no detectable adverse effects of the citric acid on the efficacy of copper sulfate.

In addition, field application studies using copper sulfate pentahydrate-citric acid monohydrate formulations of a 1:0.5 ratio and copper sulfate pentahydrate alone were performed in Lake Catherine (Antioch, Illinois). These studies indicated inhibition of precipitation in the presence of citric acid over a 24-hour period (Kothandaraman and Evans, 1980).

Particulate Adsorption

Gachter et al. (1978) and Wagemann and Barica (1978) have pointed out that adsorption of copper by solids can have a significant effect on the dissolved copper concentration. Figure 8 shows a clear comparison of percent copper remaining for a Lake Eureka sample analyzed over a period of 96 hours for both filtered and unfiltered subsamples, with and without a chelant. These results indicate a significant effect of sediments and seston on dissolved copper concentrations. In both the presence and absence of suspended sediments, the addition of citric acid enhanced the overall solubility of the copper, but a significantly higher concentration was maintained in the absence of solids. (On the order of 50% more of the initial copper remains in solution with no solids.)

These plots also indicate a levelling off of TDCu after about 48 hours. This may also be an indication of the stability of these two copper complexes, as Wagemann and Barica (1978) reported that copper concentrations in their spiked lake samples continued to follow a nearly first-order decay with steady-state concentrations attained after 10 days.

The 50% decrease in dissolved copper concentrations in the presence of suspended solids implies that adsorption plays a significant role in the loss of copper in natural waters.

Cutrine Study

A close examination of commercially available copper complexes reveals an elevated concentration of the chelating agent in most cases. This ensures high initial concentrations of the complex, allowing an advantage for the chelating agent in terms of competition for the copper once introduced into a natural system. Our examination of Cutrine, a copper/triethanolamine formulation, shows a 1:10 ratio of elemental copper to chelating agent in the concentrate. Although this represents a ratio of only 1:2.5 as copper sulfate pentahydrate to TEA, the indeterminate equilibration time afforded the formation of the complex ensures high initial concentrations. Since "tank mixing" is not allowed in Illinois, this pre-equilibration period is not available to water treatment operators unless costly commercial formulations are used. Dosage requirements listed by Applied Biochemists, the manufacturer, as indicated earlier, range from 0.4 mg/L to

1.0 mg/L as Cu^{+2}.

The laboratory Cutrine experiment involved spiking subsamples of the December 13 Lake Eureka sample with sufficient Cutrine to provide copper concentrations of 0.2, 0.5, and 0.8 mg/L as Cu^{+2}. These samples were analyzed for dissolved copper over a period of 96 hours; the results are shown in figure 9. These results also indicate a "levelling off" of the soluble copper concentration after about 48 hours. However, there is a clear benefit to using an initially high concentration of the Cu-TEA complex, as copper concentrations leveled off at much higher levels than in previous studies where pre-equilibration time was short. Although this enhances the solubility of the copper to a greater extent, the cost per treatment using Cutrine to control algal blooms is much higher than that of other current copper sulfate treatments.

Regression Analysis

The results of this study bear out a strong correlation between copper loss and pH, alkalinity, hardness, conductivity, and suspended solids. Results of a stepwise multiple regression analysis applying the above parameters to copper loss are shown in table 2. Only data from the 0.3-mg Cu/L spikes for all three lakes, both spring and summer runs, were used in this analysis. Column 1 of the table lists the dependent variables, including percent copper loss at 2 hours, percent copper loss at 24 hours, and rate of copper loss in percent/day. The second and third columns show the regression

equations for each dependent variable and the multiple correlation coefficients.

The regression equation for percent copper loss at 24 hours shows a high degree of multiple correlation ($r = 0.974$), with pH, conductivity, hardness, suspended solids, and alkalinity representing the order of decreasing significance of the independent variables. It should be noted that these equations were developed without reference to causal, biological, and physical relationships, and it is entirely possible for statistical dependence to exist without causal dependence.

SUMMARY

It is evident from the results of this study that the formation of copper complexes such as copper-citric acid and copper-TEA does slightly inhibit the precipitation of copper from natural waters. However, it is still a matter of debate as to the toxicity of these complexes in their role as algicides. Regardless of this issue, guidelines for the proper proportions of chelated copper formulations are a necessity in water treatment operations involving "on-site" preparations. This study indicates that any greater than a 1:5 (w/w) ratio of either copper sulfate pentahydrate:citric acid monohydrate or copper sulfate pentahydrate:triethanolamine results in little or no additional inhibition of copper precipitation.

Regarding the relative stability of these two formulations

in natural waters, the results indicate an initial tenacity of the citric acid complex but little staying power in comparison to the TEA formulation. Results also indicate that the enhancement of copper solubility by chelation with citric acid or TEA is not clearly evident until dissolved copper concentrations reach approximately 0.2 mg/L as Cu^{+2}. Both complexes reached comparable concentrations of dissolved copper after 24 hours, and these concentrations were higher than in those samples where chelating agents were absent. However, the adverse health effects now associated with triethanolamine seem to point to citric acid as the chelant of choice.

Suspended solids appear to play a very significant role in the loss of copper, as filtered samples retained nearly twice as much dissolved copper as corresponding unfiltered samples. Topics for further investigation might include the viability of premixing copper sulfate with chelating agents rather than making separate additions as is the case at present. Of primary importance is the debate as to the toxicity of chelated copper complexes to higher organisms and their effectiveness as algicides. This is obviously fundamental to further research in this field.

This study points to the need to carry out field scale investigations to determine the efficacy of using citric acid as a chelant within an economically and ecologically reasonable range (1:0.5 to 1:3) of copper sulfate pentahydrate to chelant ratios.

TABLES AND FIGURES

Table 1. Water Quality Characteristics of Bulk Samples

	Lake Canton		Lake Eureka		Rend Lake	
	First Run	Second Run	First Run	Second Run	First Run	Second Run
pH	7.95	8.38	7.99	8.12	7.78	7.70
Alkalinity (mg/L $CaCO_3$)	130	141	158	255	53.0	48.0
Hardness (mg/L $CaCO_3$)	190	199	240	245	87.0	92.0
Chloride (mg/L)	10.0	12.8	20.6	25.0	6.0	21.0
Sulfate (mg/L)	51.0	53.0	40.0	2.50	50.0	51.0
Suspended solids (mg/L)	28.0	11.0	23.0	42.0	19.0	17.0
Conductivity (μmho/cm)	314	413	387	562	212	286
NH_3-N (mg/L)	-	0.03	-	0.44	-	0.02
PO_4-P (mg/L)	-	0.02	-	0.22	-	0.01
Total Metal Concentrations (mg/L)						
Pb	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Cd	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Zn	0.04	0.04	0.04	0.05	0.05	0.04
Cu	0.02	0.01	0.02	<0.01	0.01	<0.01
Ca	47.0	43.0	55.0	46.0	20.0	22.0
Mg	19.0	18.0	24.0	22.0	5.6	6.0
Mn	0.08	0.07	0.07	0.14	0.21	0.37
Fe	1.70	0.38	1.00	0.13	0.33	0.24
Soluble Metal Concentrations (mg/L)						
Pb	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Cd	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Zn	0.03	0.04	0.03	0.09	0.05	0.04
Cu	0.01	0.01	0.02	<0.01	0.01	<0.01
Ca	44.0	42.0	55.0	44.0	19.0	22.0
Mg	18.0	17.0	23.0	21.0	5.4	5.8
Mn	0.01	<0.01	0.01	0.04	<0.01	<0.01
Fe	0.11	0.10	0.10	0.17	0.02	0.01

Table 2.

Regression Analysis of Copper Loss with Respect to Water Quality Parameters

Dependent Variable	Regression Equations	Multiple Corr. Coef.
Percent TDCu Loss at T=2 hr	$41.43 X_1 + 2.542 X_4 - 74.78 X_2 + 0.2331 X_3 + 0.1074 X_5 - 349.3$	0.890
Percent TDCu Loss at T=24 hr	$23.29 X_1 + 0.1822 X_5 + 0.0871 X_3 + 2.221 X_4 - 69.75 X_2 - 190.7$	0.974
ΔTDCu/Δt (%/day)	$-0.1452 X_3 + 0.0696 X_5 - 22.66 X_1 - 0.3906 X_4 + 74.28 X_2 - 194.9$	0.906

X_1 = pH (unitless)
X_2 = Alkalinity (mg/L as $CaCO_3$)
X_3 = Hardness (mg/L as $CaCO_3$)
X_4 = Suspended solids (mg/L)
X_5 = Conductivity (µmho/cm)
ΔTDCu/Δt = Rate of soluble copper loss

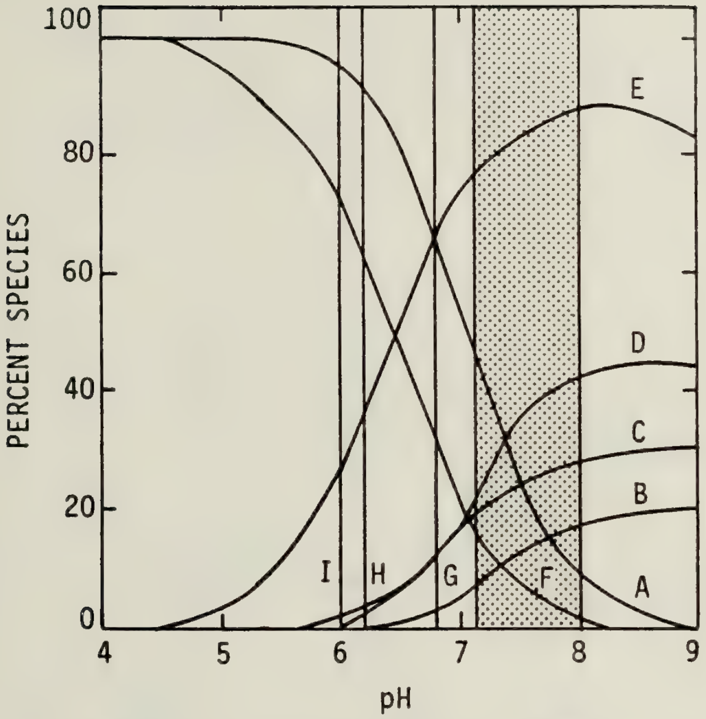


Figure 1. Speciation of copper (II) (total concentration 2 ppm) and carbonate as a function of pH (from Sylva, 1976)

Note: A=Cu^{2+}; B=$Cu_2(OH)_2^{2+}$; C=$CuOH^+$; D=$CuCO_3$; E=HCO_3^-; F=H_2CO_3; G=pH at which $Cu(OH)_2$ will precipitate; H=pH at which $Cu_3(OH)_2(CO_3)_2$ will precipitate; and I=pH at which $Cu_2(OH)_2CO_3$ will precipitate.

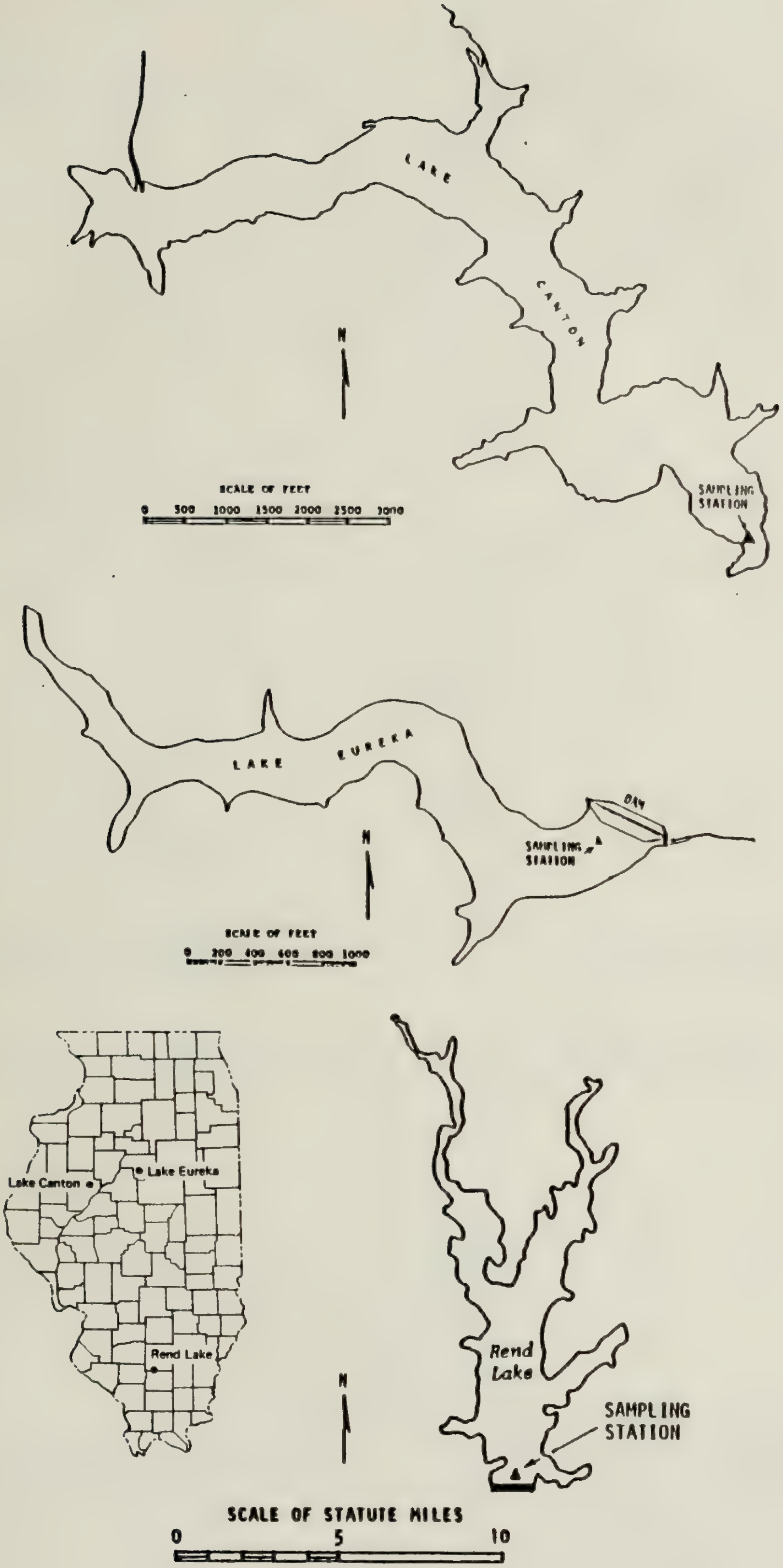


Figure 2. Sampling locations on Lake Canton, Lake Eureka, and Rend Lake

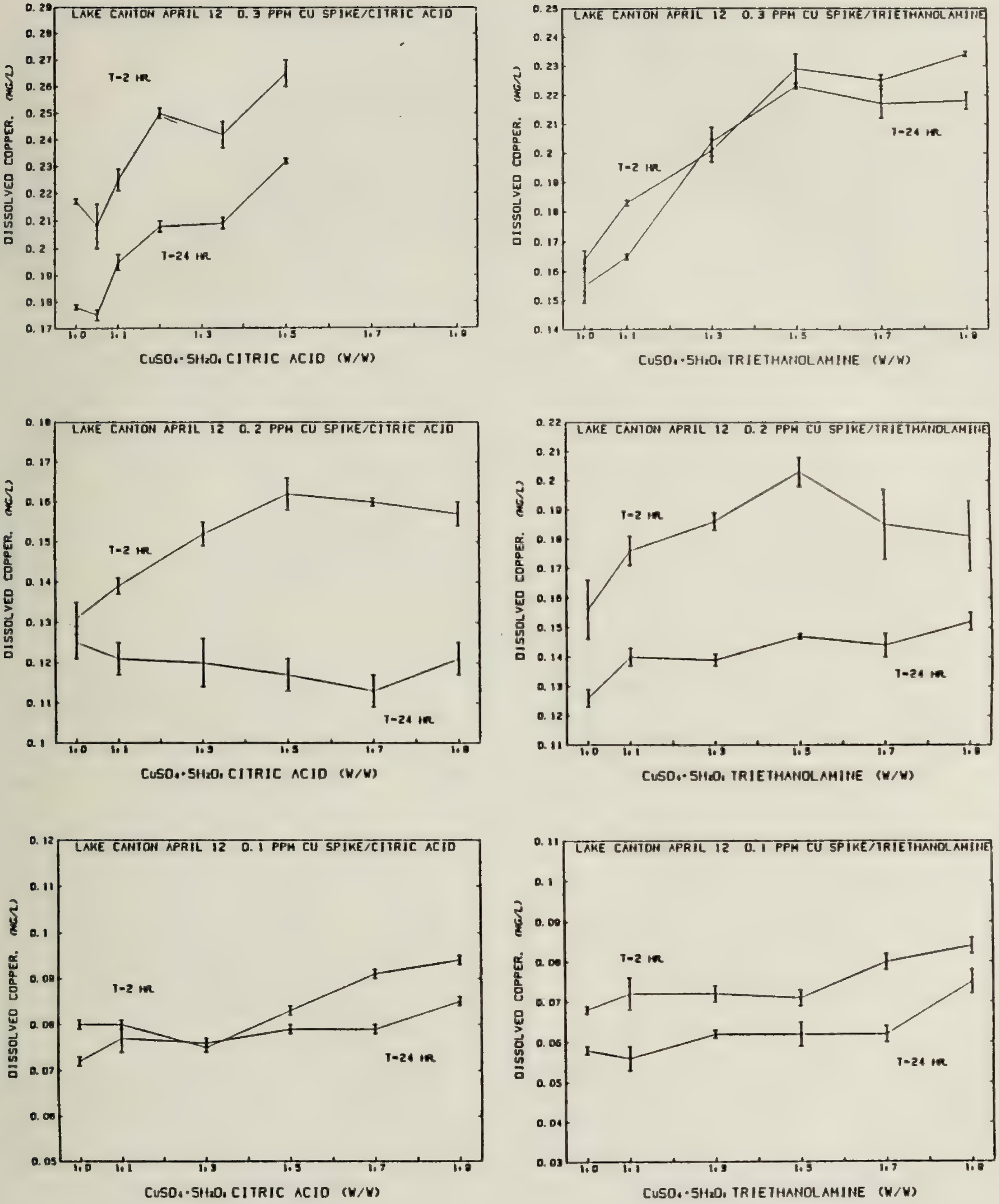


Figure 3a. Lake Canton TDCu analysis of April 12, 1985 sampling

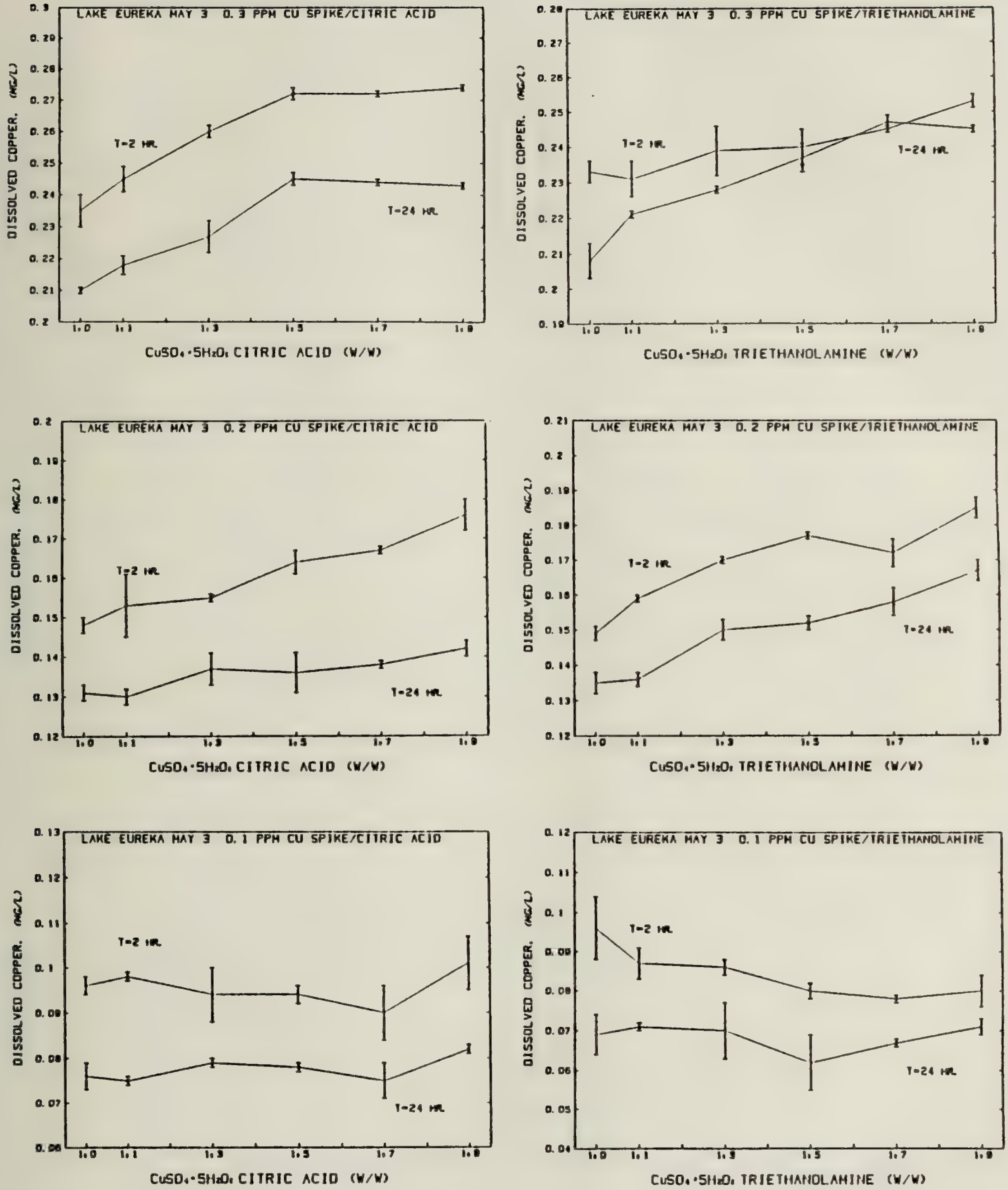


Figure 3b. Lake Eureka TDCu analysis of May 3, 1985 sampling

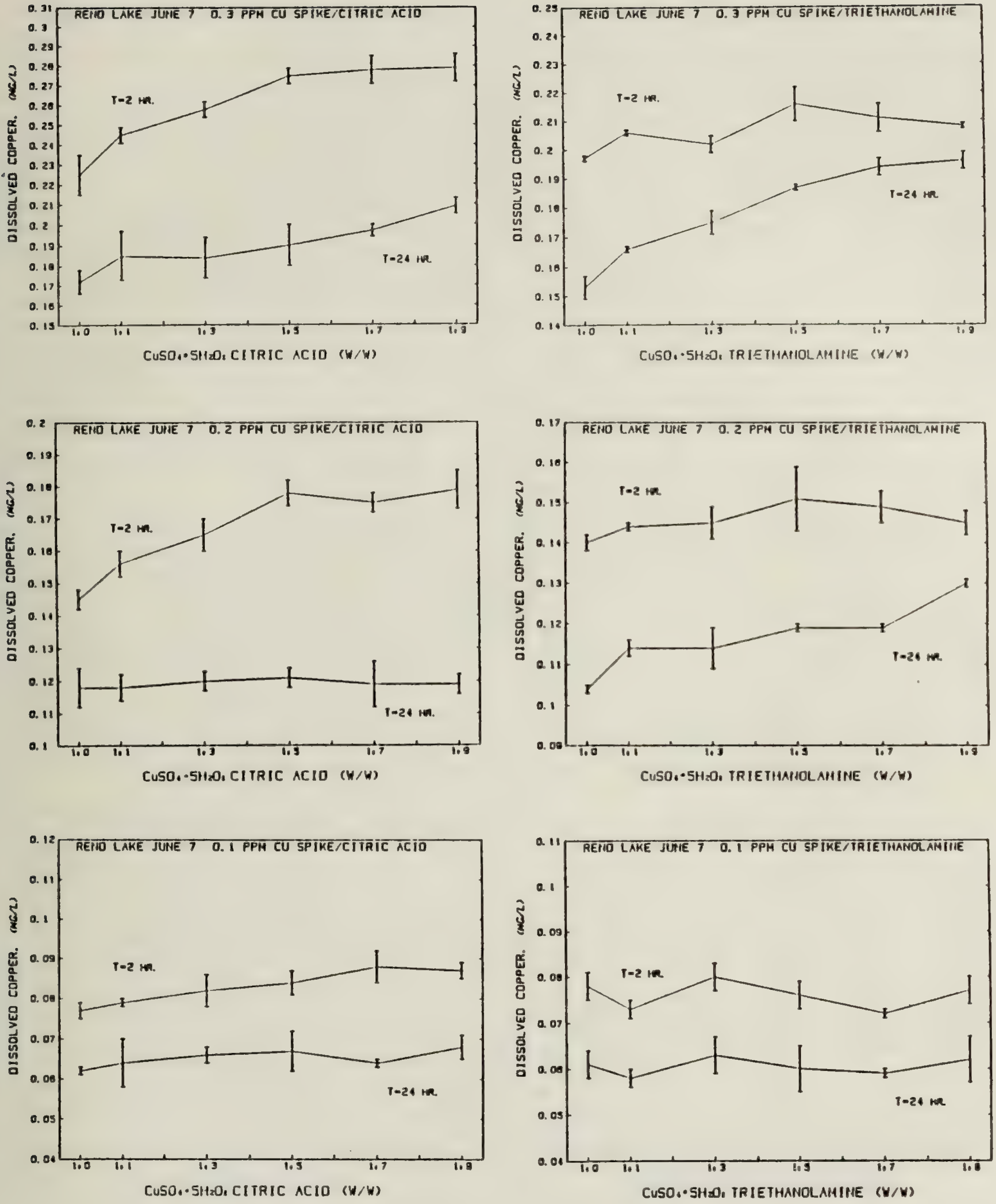


Figure 3c. Rend Lake TDCu analysis of June 7, 1985 sampling

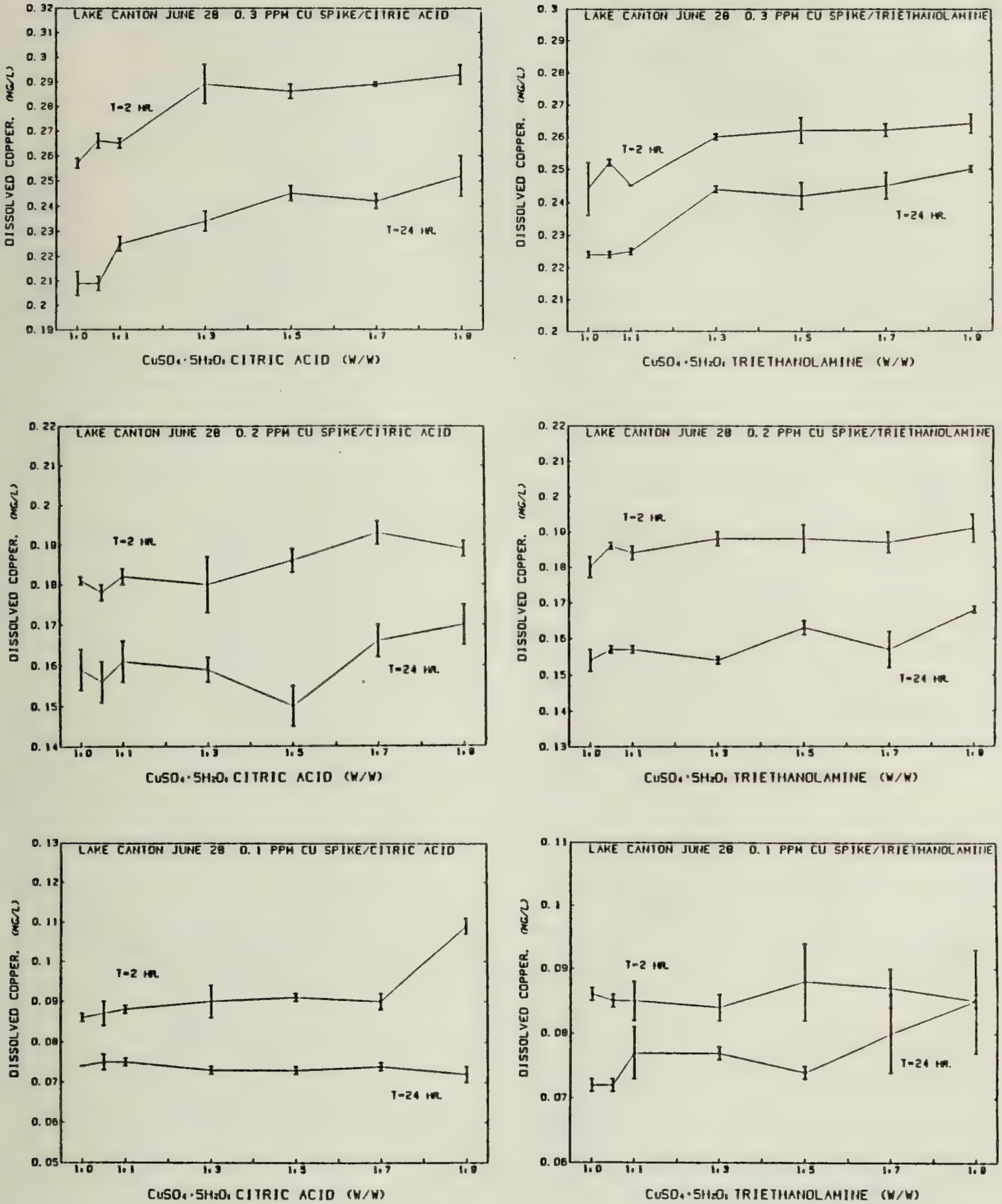


Figure 3d. Lake Canton TDCu analysis of June 28, 1985 sampling

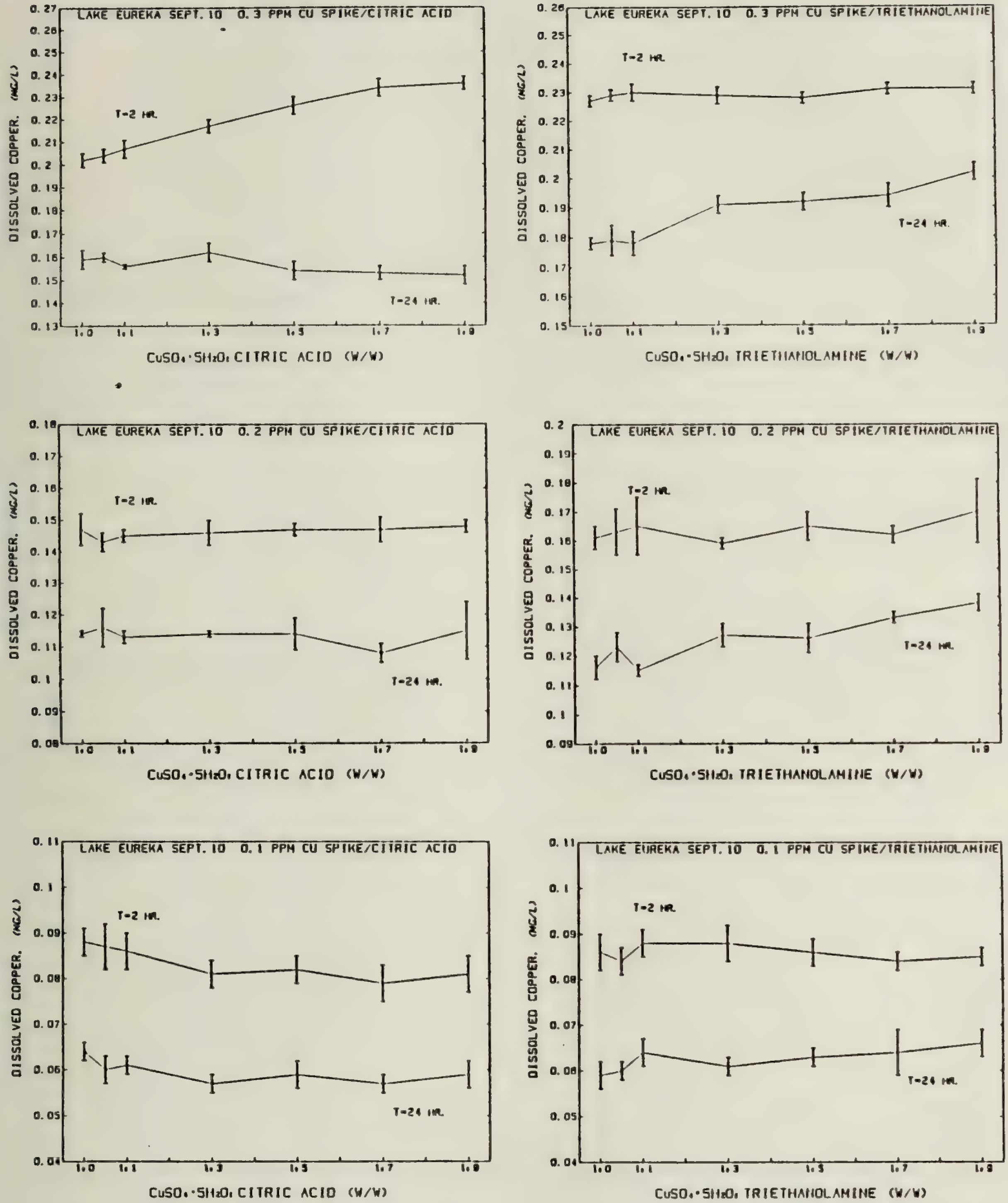


Figure 3e. Lake Eureka TDCu analysis of September 10, 1985 sampling

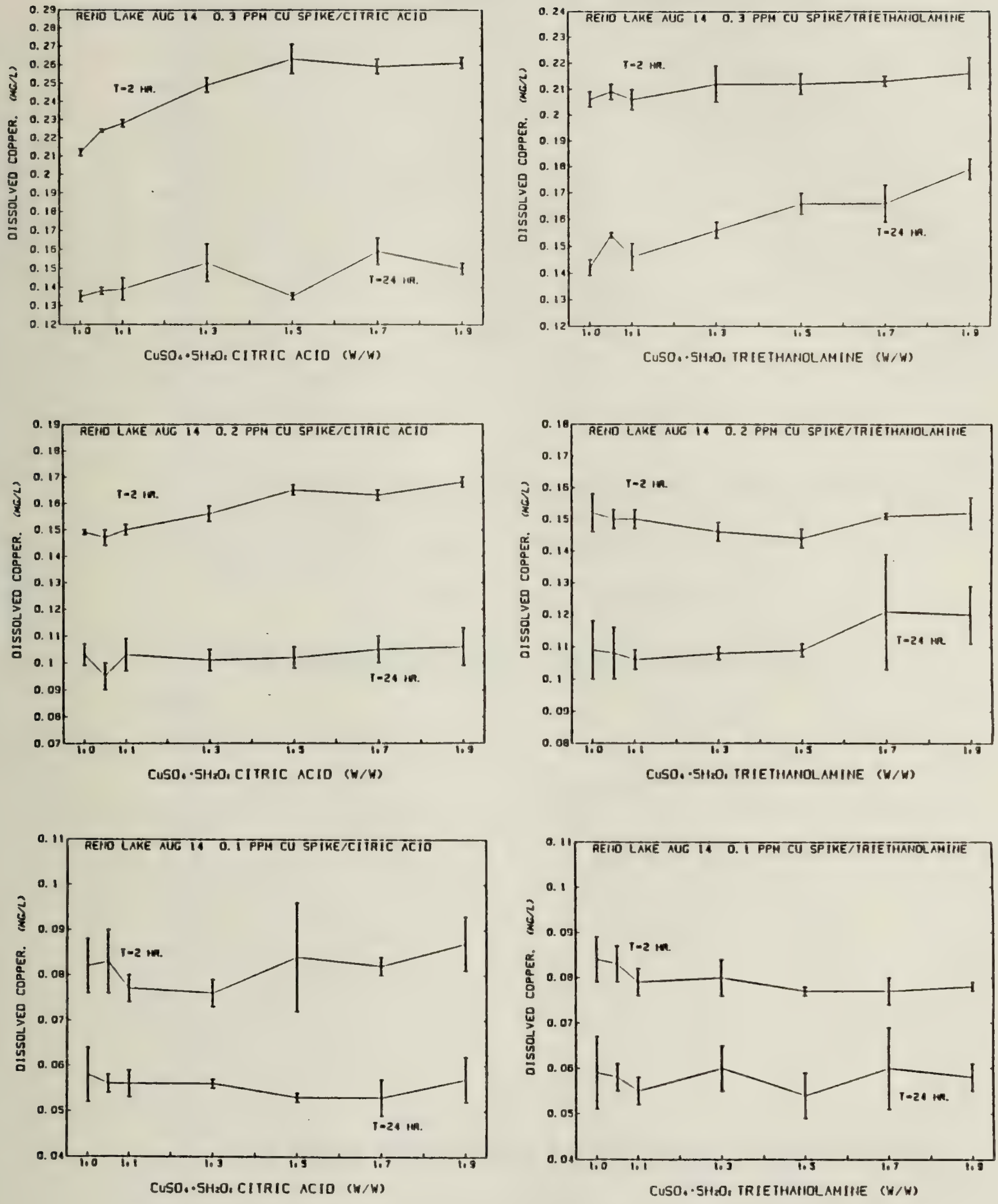
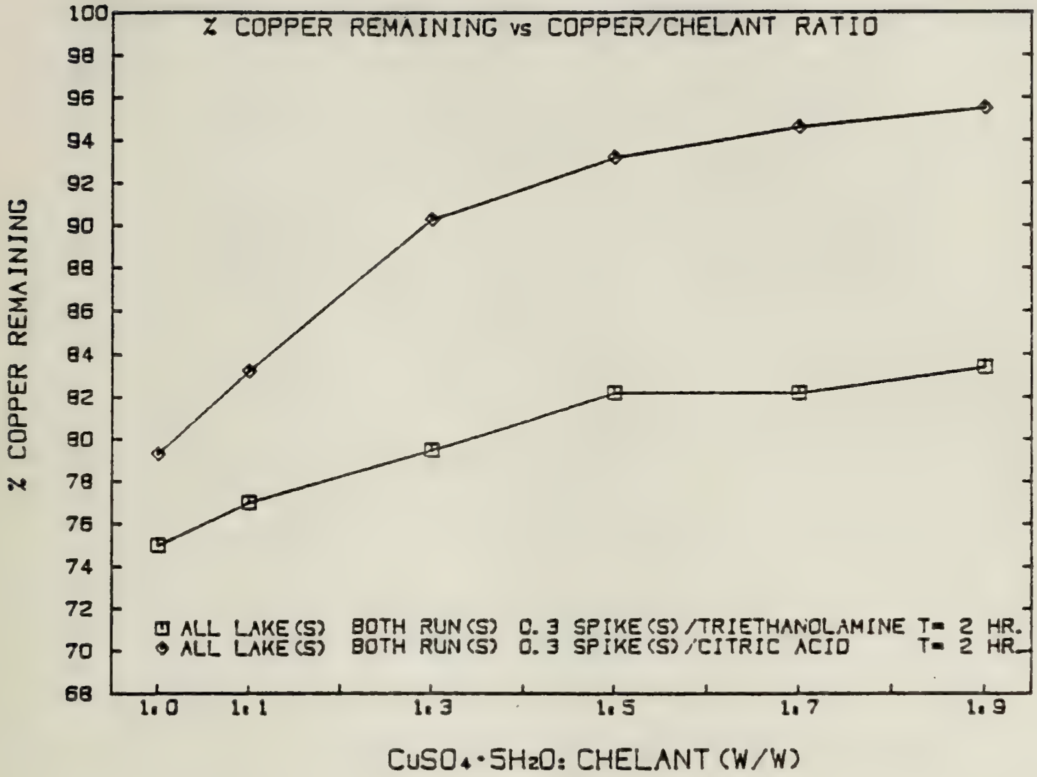


Figure 3f. Rend Lake TDCu analysis of August 14, 1985 sampling



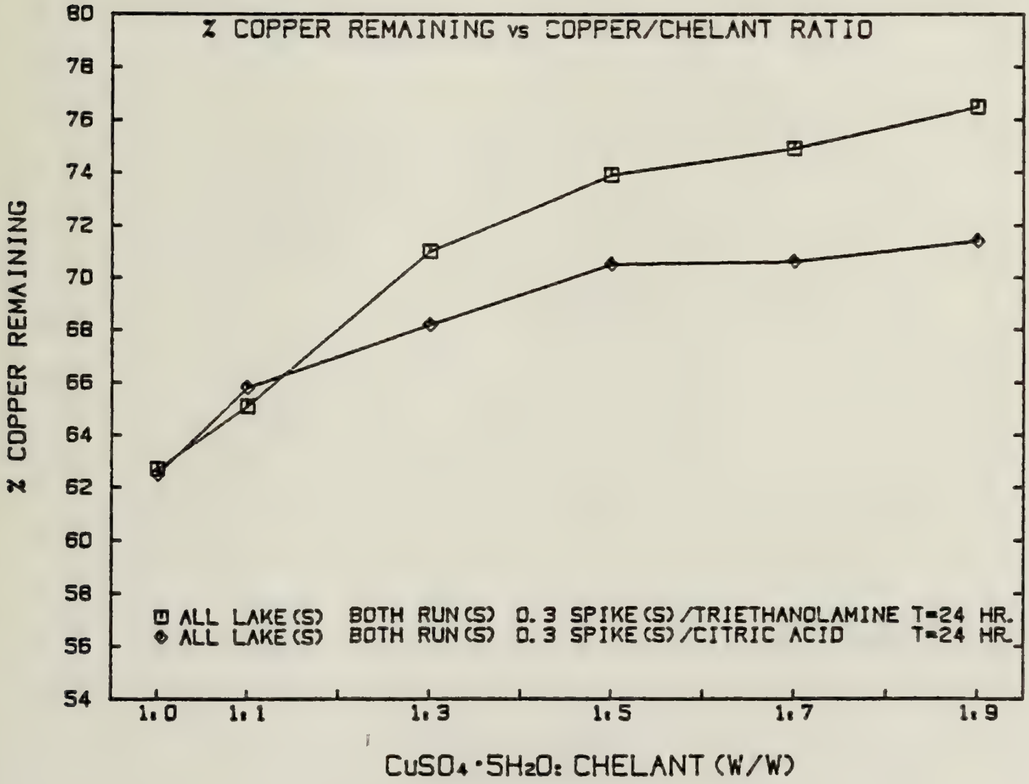


Figure 4. Average percent copper remaining in solution vs. $CuSO_4 \cdot 5H_2O$/chelant ratio (w/w) for all lakes, both runs and 0.3 mg Cu/L spike

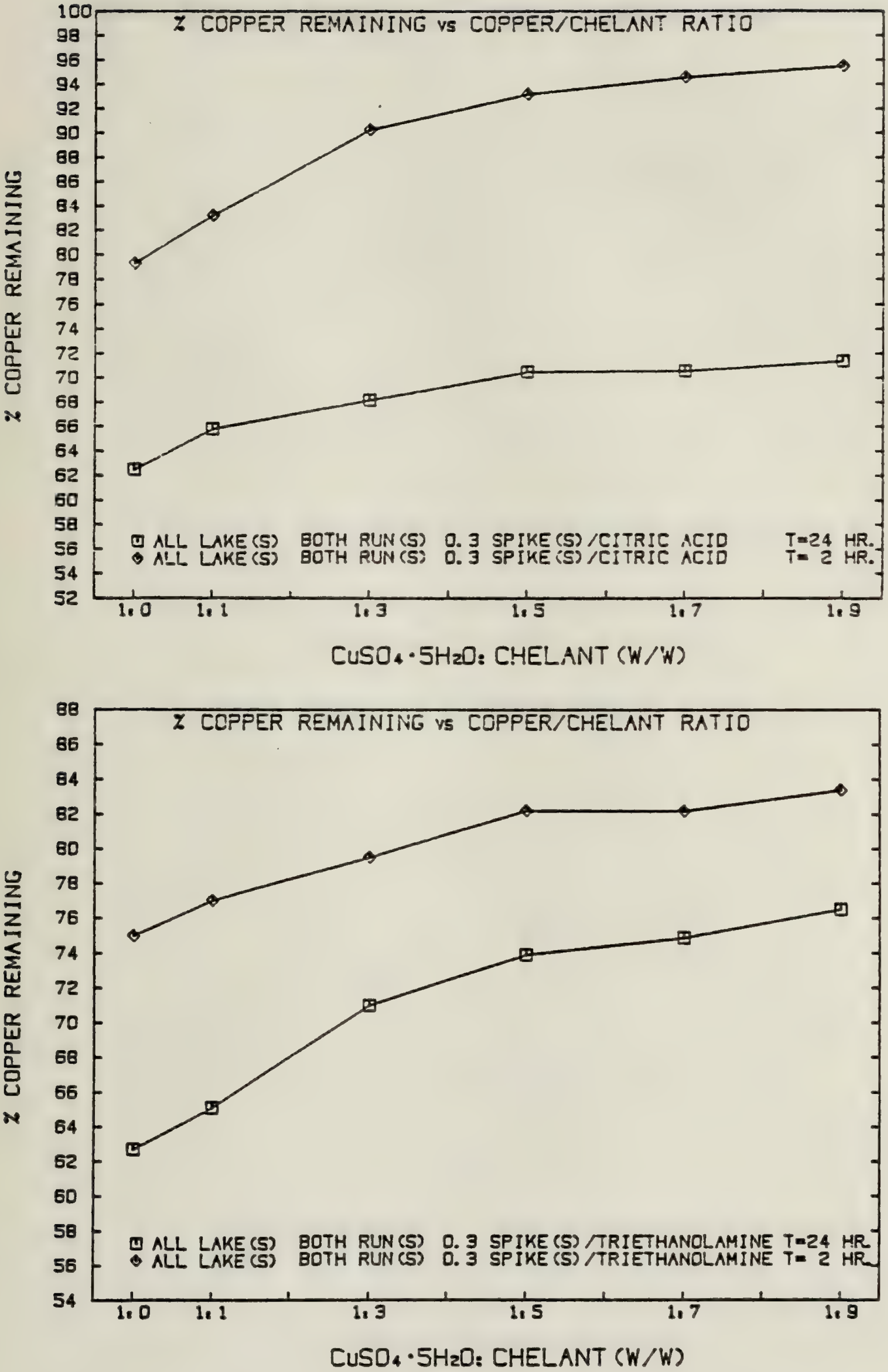


Figure 4. Concluded

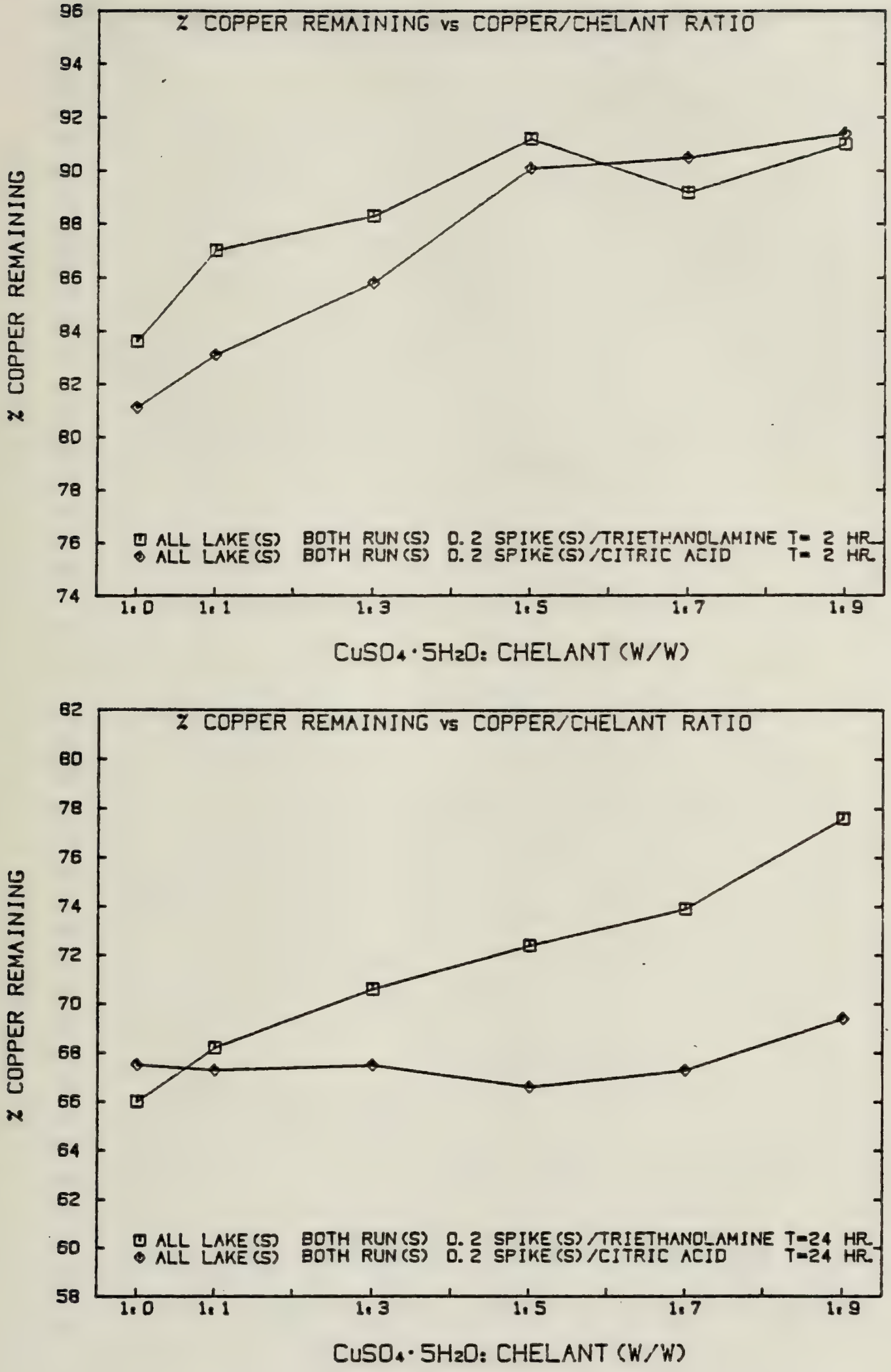


Figure 5. Average percent copper remaining in solution vs. $CuSO_4 \cdot 5H_2O$/chelant ratio (w/w) for all lakes, both runs and 0.2 mg Cu/L spike

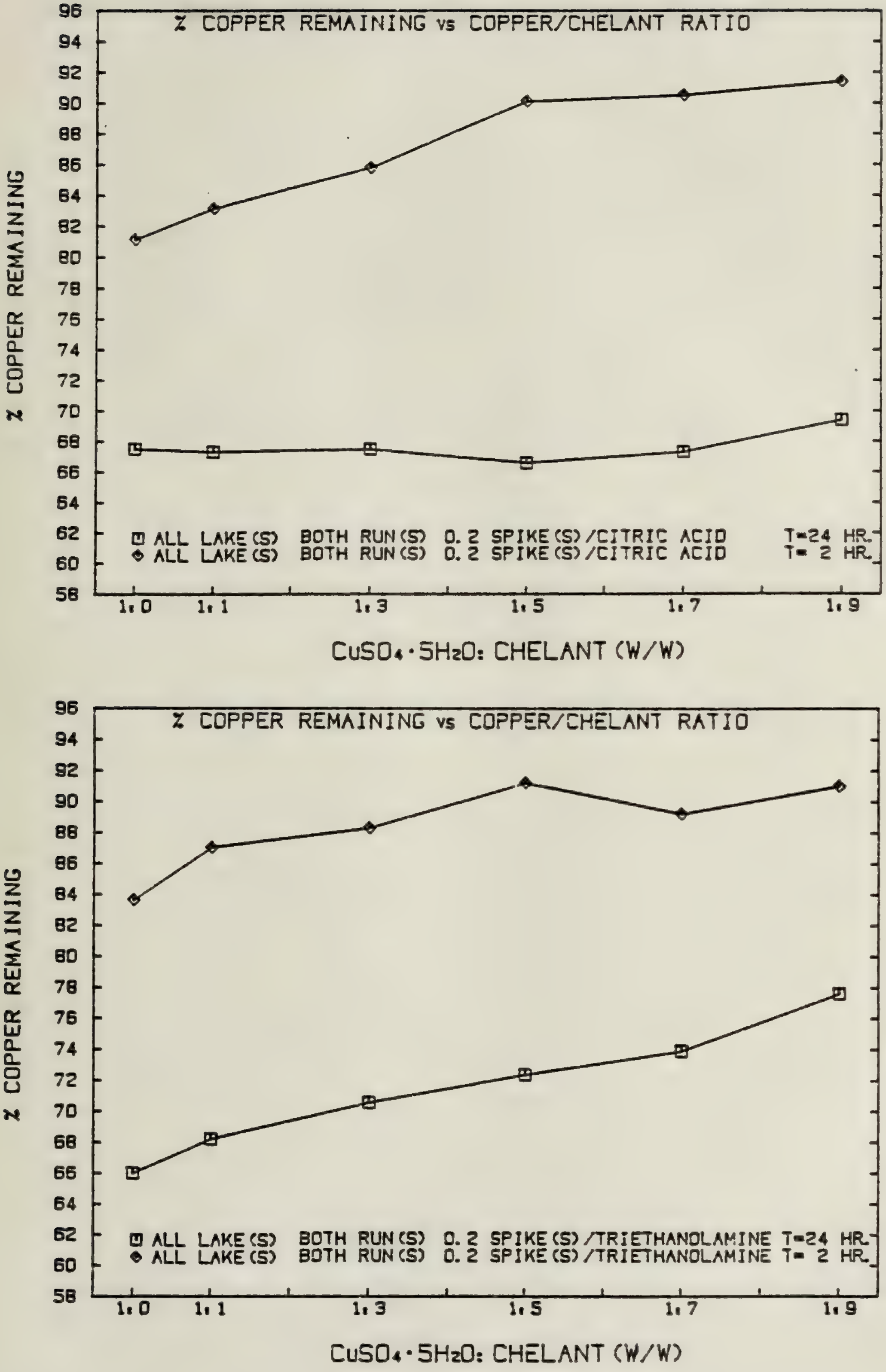


Figure 5. Concluded

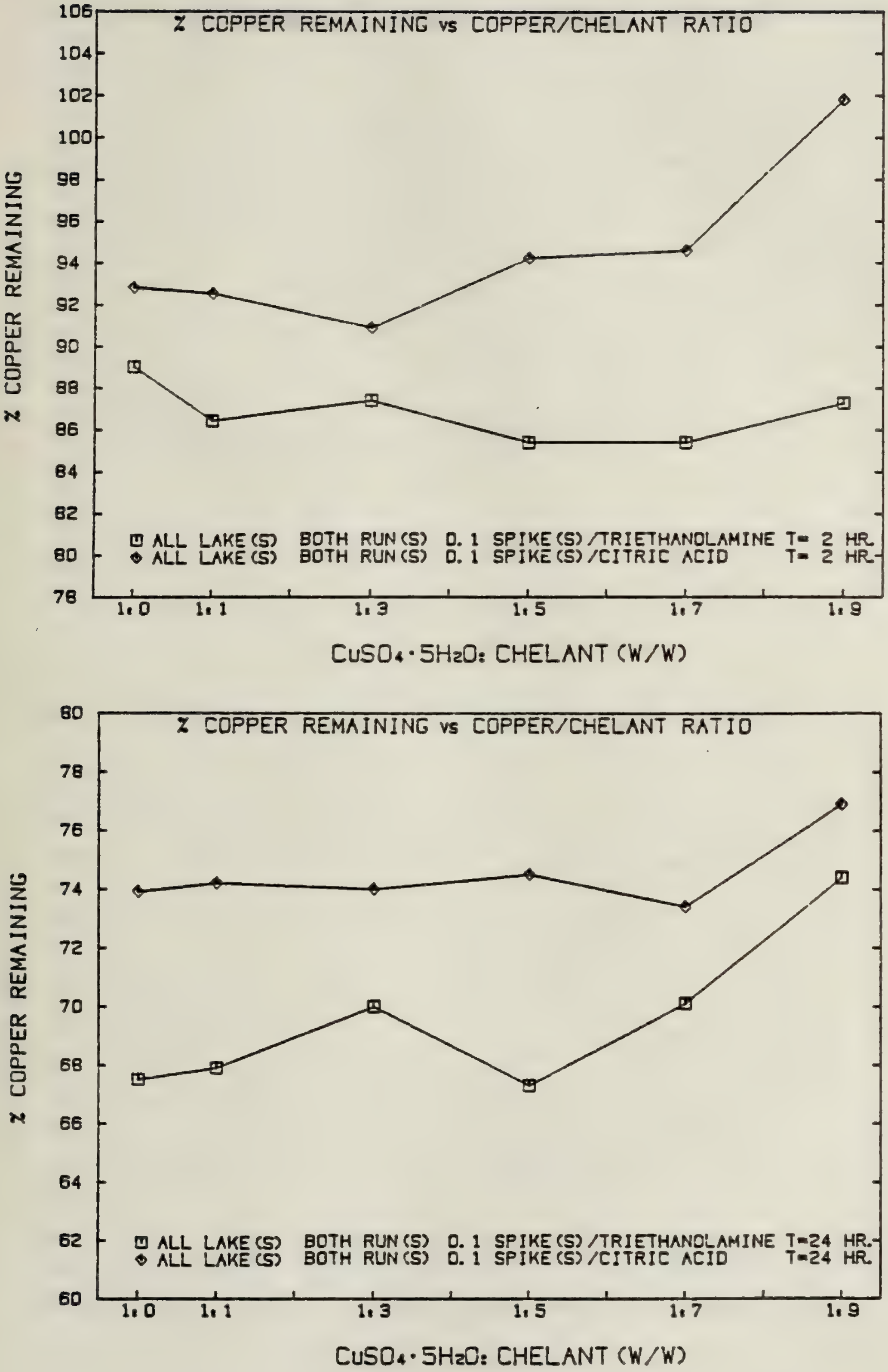


Figure 6. Average percent copper remaining in solution vs. $CuSO_4 \cdot 5H_2O$/chelant ratio (w/w) for all lakes, both runs and 0.1 mg Cu/L spike

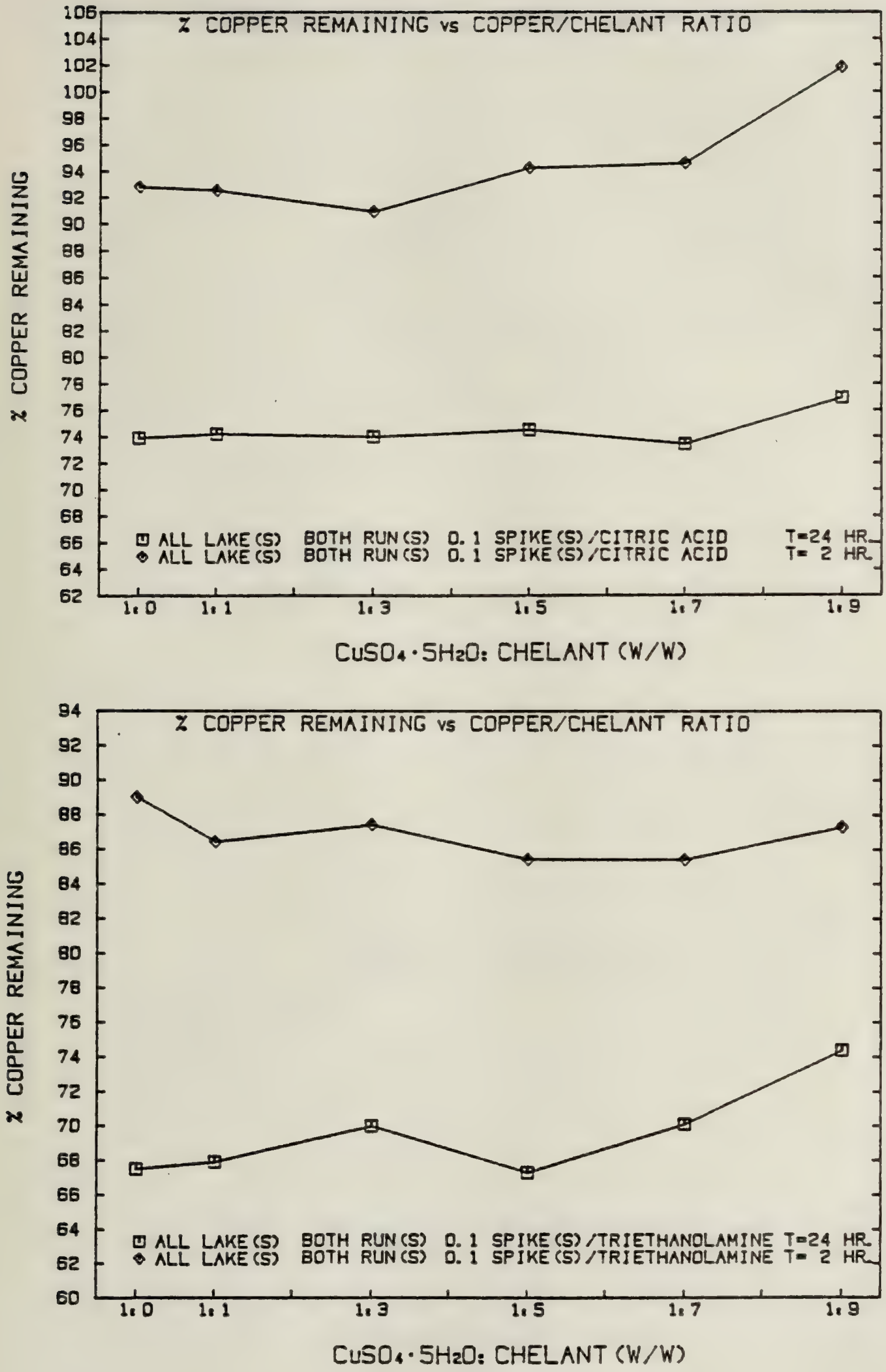


Figure 6. Concluded

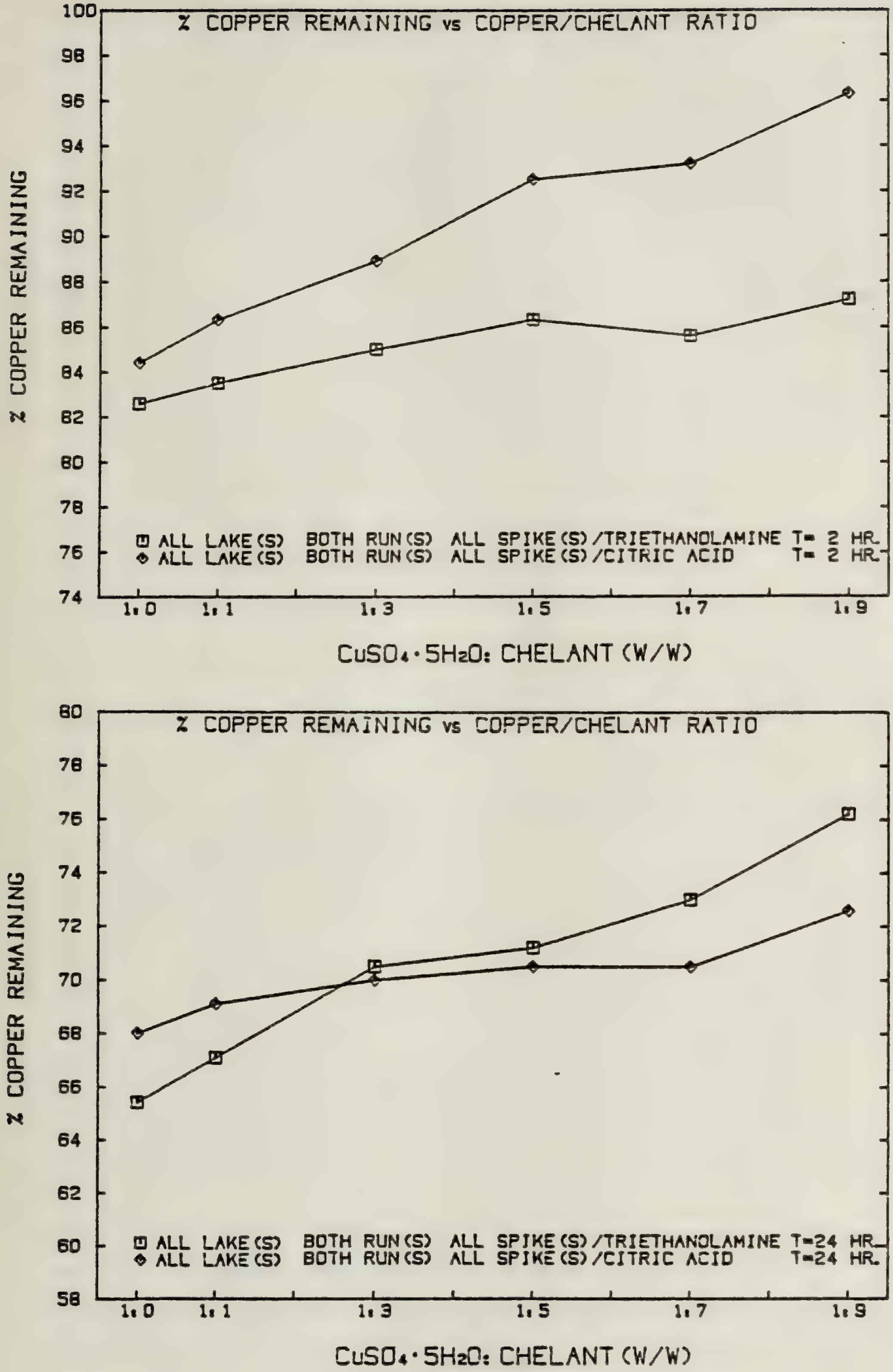
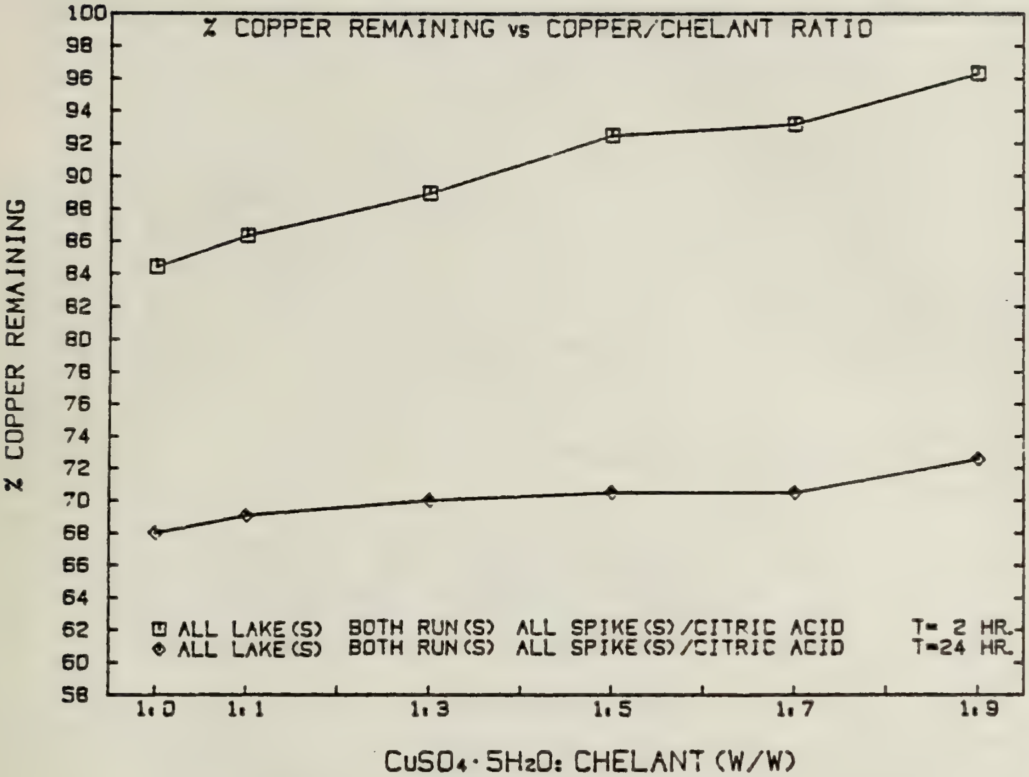


Figure 7. Average percent copper remaining in solution vs. $CuSO_4 \cdot 5H_2O$/chelant ratio (w/w) for all lakes, both runs and all spike concentrations



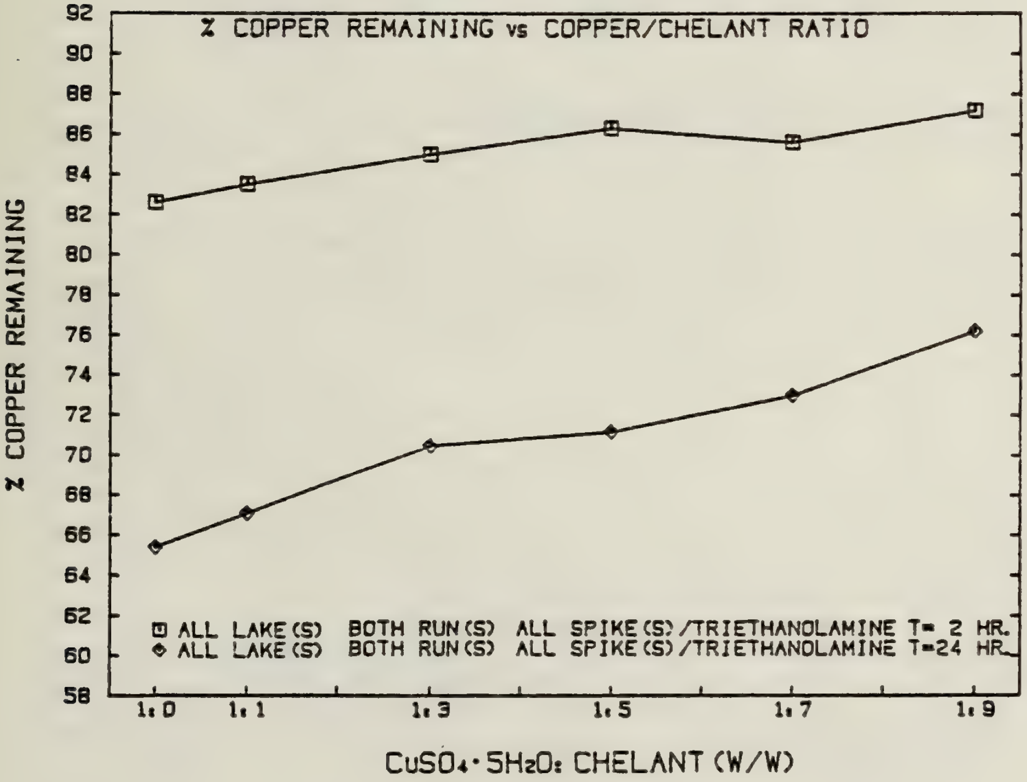


Figure 7. Concluded

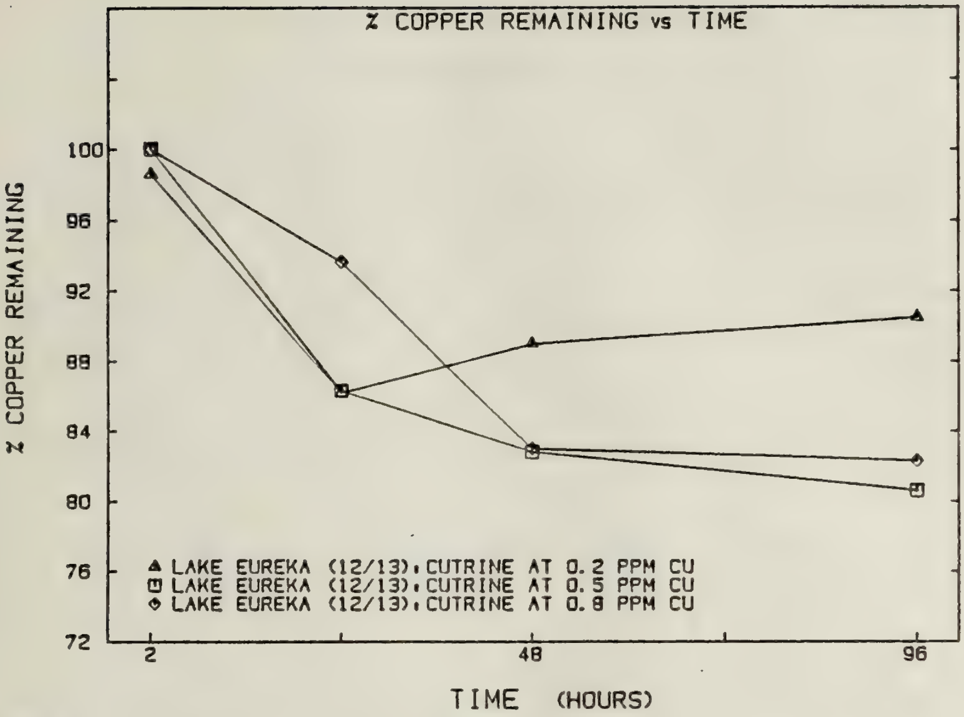


Figure 8. Comparison of filtered vs. unfiltered Lake Eureka sample with and without citric acid (Spike concentration is 0.25 mg Cu/L with $CuSO_4 \cdot 5H_2O/C_6H_8O_7 \cdot H_2O$ ratio (w/w) of 1:1.25)

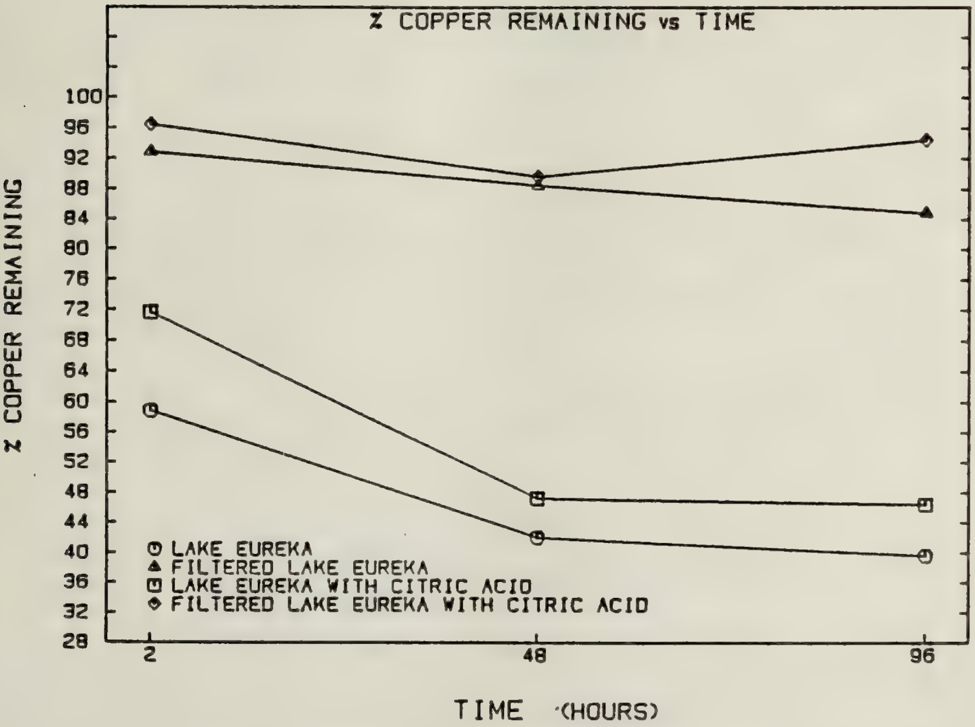


Figure 9. Percent copper remaining in solution vs. time for Cutrine dosages of 0.2, 0.5, and 0.8 mg Cu/L

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APPENDIX

Average Data for Lake Eureka - First Run (May 3, 1985)

		Citric Acid Monohydrate							Triethanolamine					
		0.3 mg/L Spike		0.2 mg/L Spike		0.1 mg/L Spike			0.3 mg/L Spike		0.2 mg/L Spike		0.1 mg/L Spike	
	Ratio[+]	TDCu[*]	%Cu REM[†]	TDCu	%Cu REM	TDCu	%Cu REM	Ratio	TDCu	%Cu REM	TDCu	%Cu REM	TDCu	%Cu REM
T=2 hr	Control	0.283	-	0.194	-	0.093	-	Control	0.295	-	0.192	-	0.092	-
	1:0.0	0.235	83.0	0.148	76.6	0.096	104	1:0.0	0.233	78.9	0.149	77.9	0.096	104
	1:1.0	0.245	86.6	0.153	78.8	0.098	106	1:1.0	0.231	78.3	0.159	83.0	0.087	94.6
	1:3.0	0.260	91.8	0.155	80.0	0.094	101	1:3.0	0.239	80.8	0.170	88.9	0.086	93.5
	1:5.0	0.272	96.2	0.164	84.7	0.094	101	1:5.0	0.240	81.2	0.177	92.3	0.080	87.0
	1:7.0	0.272	96.1	0.167	86.1	0.090	96.8	1:7.0	0.245	83.0	0.172	89.6	0.078	84.1
	1:9.0	0.274	96.8	0.176	90.7	0.101	109	1:9.0	0.253	85.8	0.185	96.5	0.080	87.0
T=24 hr	Control	0.302	-	0.193	-	0.094	-	Control	0.302	-	0.188	-	0.093	-
	1:0.0	0.210	74.1	0.131	67.5	0.076	82.0	1:0.0	0.208	70.5	0.135	70.4	0.069	74.7
	1:1.0	0.218	77.1	0.130	67.0	0.075	80.6	1:1.0	0.221	74.7	0.136	71.1	0.071	76.5
	1:3.0	0.227	80.2	0.137	70.7	0.079	85.3	1:3.0	0.228	77.3	0.150	78.4	0.070	75.5
	1:5.0	0.245	86.5	0.136	70.1	0.078	84.2	1:5.0	0.237	80.1	0.152	79.5	0.062	67.5
	1:7.0	0.244	86.2	0.138	71.3	0.075	81.3	1:7.0	0.247	83.7	0.158	82.6	0.067	72.9
	1:9.0	0.243	85.7	0.142	73.5	0.082	88.5	1:9.0	0.245	83.0	0.167	87.1	0.071	76.9

[+] Ratios are calculated on a weight/weight basis as $CuSO4 \cdot 5H_2O$/chelant

[*] TDCu represents the average total dissolved copper of triplicate trials

[†] %Cu REM represents percent dissolved copper remaining in solution vs. control

Average Data for Lake Eureka - Second Run (September 10, 1985)

	Citric Acid Monohydrate							Triethanolamine						
		0.3 mg/L Spike		0.2 mg/L Spike		0.1 mg/L Spike			0.3 mg/L Spike		0.2 mg/L Spike		0.1 mg/L Spike	
	Ratio+	TDCu*	%Cu REM†	TDCu	%Cu REM	TDCu	%Cu REM	Ratio	TDCu	%Cu REM	TDCu	%Cu REM	TDCu	%Cu REM
T=2 hr	Control	0.263	-	0.179	-	0.086	-	Control	0.276	-	0.179	-	0.090	-
	1:0.0	0.202	76.7	0.147	82.3	0.088	102	1:0.0	0.227	82.0	0.161	90.1	0.086	95.6
	1:0.5	0.204	77.4	0.143	80.1	0.087	101	1:0.5	0.229	82.8	0.163	91.4	0.084	92.4
	1:1.0	0.207	78.6	0.145	81.0	0.086	99.6	1:1.0	0.230	83.4	0.165	92.5	0.088	96.9
	1:3.0	0.217	82.3	0.146	81.5	0.081	94.0	1:3.0	0.229	82.9	0.159	89.2	0.088	96.9
	1:5.0	0.226	85.7	0.147	82.0	0.082	95.2	1:5.0	0.228	82.7	0.165	92.4	0.086	95.0
	1:7.0	0.234	88.8	0.147	82.3	0.079	91.3	1:7.0	0.231	83.5	0.162	90.7	0.084	92.6
	1:9.0	0.236	89.7	0.148	82.8	0.081	93.8	1:9.0	0.231	83.6	0.170	95.0	0.085	94.1
T=24 hr	Control	0.320	-	0.158	-	0.089	-	Control	0.268	-	0.182	-	0.087	-
	1:0.0	0.159	60.5	0.114	63.6	0.064	73.6	1:0.0	0.178	64.3	0.116	65.0	0.059	64.8
	1:0.5	0.160	60.8	0.116	64.8	0.060	69.1	1:0.5	0.179	64.9	0.123	68.8	0.060	66.4
	1:1.0	0.156	59.4	0.113	63.4	0.061	70.1	1:1.0	0.178	64.6	0.115	64.6	0.064	70.3
	1:3.0	0.162	61.4	0.114	64.0	0.057	66.4	1:3.0	0.191	69.2	0.127	70.8	0.061	67.3
	1:5.0	0.154	58.4	0.114	63.7	0.059	68.1	1:5.0	0.192	69.3	0.126	70.3	0.063	70.1
	1:7.0	0.153	58.2	0.108	60.6	0.057	66.2	1:7.0	0.194	70.1	0.133	74.6	0.064	70.7
	1:9.0	0.152	57.6	0.115	64.3	0.059	68.0	1:9.0	0.202	73.1	0.138	77.1	0.066	72.7

+ Ratios are calculated on a weight/weight basis as $CuSO_4 \cdot 5H_2O$/chelant

* TDCu represents the average total dissolved copper of triplicate trials

† %Cu REM represents percent dissolved copper remaining in solution vs. control

Average Data for Lake Canton - First Run (April 12, 1985)

	Citric Acid Monohydrate							Triethanolamine						
		0.3 mg/L Spike		0.2 mg/L Spike		0.1 mg/L Spike			0.3 mg/L Spike		0.2 mg/L Spike		0.1 mg/L Spike	
	Ratio[+]	TDCu[*]	%Cu REM[†]	TDCu	%Cu REM	TDCu	%Cu REM	Ratio	TDCu	%Cu REM	TDCu	%Cu REM	TDCu	%Cu REM
T=2 hr	Control	0.295	-	0.171	-	0.093	-	Control	0.263	-	0.203	-	0.093	-
	1:0.0	0.217	73.6	0.131	76.8	0.080	86.3	1:0.0	0.164	62.3	0.156	77.0	0.068	77.5
	1:0.5	0.208	70.5	-	-	-	-	1:0.5	-	-	-	-	-	-
	1:1.0	0.225	76.4	0.139	81.5	0.080	86.0	1:1.0	0.183	69.5	0.176	86.7	0.072	77.5
	1:2.0	0.250	84.7	-	-	-	-	1:2.0	-	-	-	-	-	-
	1:3.0	-	-	0.152	88.9	0.075	81.3	1:3.0	0.201	76.2	0.186	91.5	0.072	77.5
	1:3.5	0.242	82.1	-	-	-	-	1:3.5	-	-	-	-	-	-
	1:5.0	0.265	90.0	0.162	94.9	0.083	89.2	1:5.0	0.229	87.1	0.203	100.0	0.071	76.4
	1:7.0	-	-	0.160	93.8	0.041	98.2	1:7.0	0.225	85.6	0.185	91.0	0.080	85.4
	1:9.0	-	-	0.157	91.6	0.094	101.4	1:9.0	0.234	88.9	0.181	89.3	0.084	90.4
T=24 hr	Control	0.269	-	0.191	-	0.096	-	Control	0.291	-	0.178	-	0.091	-
	1:0.0	0.178	60.3	0.125	72.9	0.072	77.7	1:0.0	0.155	58.7	0.126	61.9	0.058	62.1
	1:0.5	0.175	59.5	-	-	-	-	1:0.5	-	-	-	-	-	-
	1:1.0	0.195	66.1	0.121	71.0	0.077	83.1	1:1.0	0.165	62.5	0.140	69.0	0.056	60.0
	1:2.0	0.208	70.5	-	-	-	-	1:2.0	-	-	-	-	-	-
	1:3.0	-	-	0.120	70.0	0.076	81.7	1:3.0	0.204	77.5	0.139	68.3	0.062	66.8
	1:3.5	0.209	70.8	-	-	-	-	1:3.5	-	-	-	-	-	-
	1:5.0	0.232	78.6	0.117	68.6	0.079	85.3	1:5.0	0.223	84.7	0.147	72.6	0.062	66.4
	1:7.0	-	-	0.113	66.3	0.079	85.6	1:7.0	0.217	82.5	0.144	70.9	0.062	66.8
	1:9.0	-	-	0.121	70.6	0.085	91.4	1:9.0	0.218	82.9	0.152	74.9	0.075	79.8

[+] Ratios are calculated on a weight/weight basis as $CuSO_4 \cdot 5H_2O$/chelant

[*] TDCu represents the average total dissolved copper of triplicate trials

[†] %Cu REM represents percent dissolved copper remaining in solution vs. control

Average Data for Lake Canton - Second Run (June 28, 1985)

		Citric Acid Monohydrate							Triethanolamine					
		0.3 mg/L Spike		0.2 mg/L Spike		0.1 mg/L Spike			0.3 mg/L Spike		0.2 mg/L Spike		0.1 mg/L Spike	
	Ratio+	TDCu*	%Cu REM†	TDCu	%Cu REM	TDCu	%Cu REM	Ratio	TDCu	%Cu REM	TDCu	%Cu REM	TDCu	%Cu REM
T=2 hr	Control	0.283	-	0.188	-	0.088	-	Control	0.281	-	0.187	-	0.091	-
	1:0.0	0.257	91.0	0.181	96.3	0.086	97.4	1:0.0	0.244	86.7	0.180	96.4	0.086	95.2
	1:0.5	0.266	94.1	0.178	94.5	0.087	98.5	1:0.5	0.252	89.6	0.186	99.6	0.085	93.8
	1:1.0	0.265	93.9	0.182	96.6	0.088	99.2	1:1.0	0.245	87.2	0.184	98.6	0.085	93.8
	1:3.0	0.289	102	0.180	95.7	0.090	101	1:3.0	0.260	92.6	0.188	101	0.084	92.3
	1:5.0	0.286	101	0.186	98.9	0.091	103	1:5.0	0.262	93.4	0.188	101	0.088	96.7
	1:7.0	0.289	102	0.193	103	0.090	102	1:7.0	0.262	93.4	0.187	100	0.087	96.3
	1:9.0	0.293	104	0.189	101	0.109	123	1:9.0	0.264	94.1	0.191	102	0.085	93.8
T=24 hr	Control	0.283	-	0.188	-	0.085	-	Control	0.283	-	0.179	-	0.090	-
	1:0.0	0.209	73.9	0.159	84.6	0.074	83.8	1:0.0	0.224	79.8	0.154	82.2	0.072	79.8
	1:0.5	0.209	73.9	0.156	82.8	0.075	84.5	1:0.5	0.224	79.8	0.157	83.8	0.072	79.4
	1:1.0	0.225	79.6	0.161	85.8	0.075	84.9	1:1.0	0.225	8.01	0.157	84.1	0.077	84.6
	1:3.0	0.234	82.8	0.159	84.6	0.073	82.3	1:3.0	0.244	86.8	0.154	82.4	0.077	84.6
	1:5.0	0.245	86.7	0.150	79.8	0.073	82.3	1:5.0	0.242	86.1	0.163	87.0	0.074	82.0
	1:7.0	0.242	85.5	0.166	88.3	0.074	83.8	1:7.0	0.245	87.1	0.157	84.1	0.080	87.9
	1:9.0	0.252	89.0	0.170	90.6	0.072	81.1	1:9.0	0.250	89.0	0.168	89.7	0.085	93.8

+ Ratios are calculated on a weight/weight basis as $CuSO_4 \cdot 5H_2O$/chelant

* TDCu represents the average total dissolved copper of triplicate trials

† %Cu REM represents percent dissolved copper remaining in solution vs. control

Average Data for Rend Lake - First Run (June 7, 1985)

	Citric Acid Monohydrate							Triethanolamine					
		0.3 mg/L Spike		0.2 mg/L Spike		0.1 mg/L Spike			0.3 mg/L Spike		0.2 mg/L Spike		0.1 mg/L Spike	
	Ratio$^+$	TDCu*	%Cu REM†	TDCu	%Cu REM	TDCu	%Cu REM	Ratio	TDCu	%Cu REM	TDCu	%Cu REM	TDCu	%Cu REM
T=2 hr	Control	0.281	-	0.185	-	0.092	-	Control	0.279	-	0.182	-	0.096	-
	1:0.0	0.225	80.1	0.145	78.1	0.077	84.1	1:0.0	0.197	70.4	0.140	77.1	0.078	81.6
	1:1.0	0.245	87.2	0.156	83.9	0.079	86.2	1:1.0	0.206	73.7	0.144	79.1	0.073	76.0
	1:3.0	0.258	91.9	0.165	89.0	0.082	89.5	1:3.0	0.202	72.4	0.145	79.5	0.080	83.3
	1:5.0	0.275	97.8	0.178	95.9	0.084	91.7	1:5.0	0.216	77.2	0.151	82.8	0.076	79.5
	1:7.0	0.278	98.8	0.175	94.5	0.088	95.3	1:7.0	0.211	75.4	0.149	81.9	0.072	75.3
	1:9.0	0.279	99.5	0.179	96.3	0.087	94.0	1:9.0	0.208	74.6	0.145	79.9	0.077	79.9
T=24 hr	Control	0.284	-	0.205	-	0.093	-	Control	0.281	-	0.180	-	0.092	-
	1:0.0	0.172	61.3	0.118	63.7	0.062	67.8	1:0.0	0.153	54.8	0.104	57.1	0.061	63.2
	1:1.0	0.185	65.9	0.118	63.6	0.064	69.9	1:1.0	0.166	59.5	0.114	62.5	0.058	60.8
	1:3.0	0.184	65.4	0.120	64.6	0.066	71.4	1:3.0	0.175	62.5	0.114	62.5	0.063	65.3
	1:5.0	0.190	67.5	0.121	65.2	0.067	73.2	1:5.0	0.187	66.8	0.119	65.4	0.060	62.8
	1:7.0	0.197	70.2	0.119	63.9	0.064	69.6	1:7.0	0.194	69.5	0.119	65.4	0.059	61.8
	1:9.0	0.209	74.5	0.118	63.4	0.068	73.9	1:9.0	0.196	70.2	0.130	71.4	0.062	64.2

+ Ratios are calculated on a weight/weight basis as $CuSO_4 \cdot 5H_2O$/chelant

* TDCu represents the average total dissolved copper of triplicate trials

† %Cu REM represents percent dissolved copper remaining in solution vs. control

Average Data for Rend Lake - Second Run (August 14, 1985)

		Citric Acid Monohydrate							Triethanolamine					
		0.3 mg/L Spike		0.2 mg/L Spike		0.1 mg/L Spike			0.3 mg/L Spike		0.2 mg/L Spike		0.1 mg/L Spike	
	Ratio+	TDCu*	%Cu REM†	TDCu	%Cu REM	TDCu	%Cu REM	Ratio	TDCu	%Cu REM	TDCu	%Cu REM	TDCu	%Cu REM
T=2 hr	Control	0.297	-	0.195	-	0.098	-	Control	0.293	-	0.182	-	0.098	-
	1:0.0	0.212	71.4	0.149	76.7	0.082	83.5	1:0.0	0.206	70.2	0.152	83.5	0.084	85.2
	1:0.5	0.224	75.5	0.147	75.7	0.083	85.2	1:0.5	0.209	71.3	0.150	82.4	0.083	84.4
	1:1.0	0.228	76.7	0.150	77.1	0.077	78.4	1:1.0	0.206	70.3	0.150	82.4	0.079	80.1
	1:3.0	0.249	83.8	0.156	80.0	0.076	78.0	1:3.0	0.212	72.3	0.146	80.0	0.080	81.0
	1:5.0	0.263	88.4	0.165	84.5	0.084	85.3	1:5.0	0.212	72.1	0.144	79.2	0.077	77.9
	1:7.0	0.259	87.2	0.163	83.9	0.082	84.2	1:7.0	0.213	72.5	0.151	82.6	0.077	78.8
	1:9.0	0.261	88.0	0.168	86.4	0.087	89.3	1:9.0	0.216	73.7	0.152	83.2	0.078	79.1
T=24 hr	Control	0.291	-	0.200	-	0.096	-	Control	0.283	-	0.167	-	0.096	-
	1:0.0	0.135	45.3	0.130	52.7	0.058	58.6	1:0.0	0.142	48.6	0.109	59.9	0.059	60.4
	1:0.5	0.138	46.3	0.095	48.8	0.056	56.9	1:0.5	0.154	52.6	0.108	59.4	0.058	58.7
	1:1.0	0.139	46.8	0.103	53.0	0.056	56.9	1:1.0	0.146	49.7	0.106	58.0	0.055	55.5
	1:3.0	0.153	51.5	0.101	51.6	0.056	56.9	1:3.0	0.156	53.1	0.108	59.4	0.060	60.8
	1:5.0	0.135	45.3	0.102	52.6	0.053	54.3	1:5.0	0.166	56.7	0.109	60.0	0.054	55.2
	1:7.0	0.159	53.4	0.105	53.9	0.053	54.3	1:7.0	0.166	56.7	0.121	66.3	0.060	61.0
	1:9.0	0.150	50.4	0.106	54.4	0.057	58.6	1:9.0	0.179	61.2	0.120	65.9	0.058	59.3

+ Ratios are calculated on a weight/weight basis as $CuSO_4 \cdot 5H_2O$/chelant

* TDCu represents the average total dissolved copper of triplicate trials

† %Cu REM represents percent dissolved copper remaining in solution vs. control

Average Data for Filtered and Unfiltered Lake Eureka

	T=2 hr		T=48 hr		T=96 hr	
	TDCu	%Cu REM	TDCu	%Cu REM	TDCu	%Cu REM
Lake Eureka*	0.147	58.8	0.104	41.6	0.099	39.7
Lake Eureka (Citric Acid)**	0.179	71.6	0.118	47.2	0.117	46.8
Filtered Lake Eureka*	0.232	92.8	0.221	88.4	0.212	84.8
Filtered Lake Eureka (Citric Acid)**	0.241	96.4	0.224	89.6	0.236	94.4

* Samples were spiked with sufficient $CuSO_4 \cdot 5H_2O$ to provide 0.250 mg/L as Cu^{+2}

** Copper spike was premixed with sufficient citric acid monohydrate to provide a 1:1.25 (W/W) ratio of $CuSO_4 \cdot 5H_2O$ to $C_6H_8O_7 \cdot H_2O$

Average Data for Cutrine$_R$ Analysis

	T=2 hr		T=24 hr		T=48 hr		T=96 hr	
	TDCu	%Cu REM	TDCu	%Cu REM	TDCu	%Cu REM	TDCu	%Cu REM
Lake Eureka (a)	0.207	98.6	0.181	86.2	0.187	89.0	0.190	90.5
Lake Eureka (b)	0.540	100	0.463	86.3	0.444	82.8	0.432	80.6
Lake Eureka (c)	0.810	100	0.751	93.6	0.666	83.0	0.660	82.3

(a) Spiked with sufficient Cutrine to provide approximately 0.2 mg/L as Cu^{+2} (0.210 mg/L)
(b) Spiked with sufficient Cutrine to provide approximately 0.5 mg/L as Cu^{+2} (0.536 mg/L)
(c) Spiked with sufficient Cutrine to provide approximately 0.8 mg/L as Cu^{+2} (0.802 mg/L)

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16. Abstract (Limit: 200 words)

Taste and odor problems that plague waterworks using impoundments as a source can most often be attributed to algal blooms, mainly blue-greens (Sigworth, 1957). These taste and odor problems are compounded by other problems such as reduced filter runs, increased chemical costs, etc. Physical solutions to the problems such as harvesting of algae or control of excessive nutrient inputs can be extremely costly and time consuming in comparison to chemical methods of bloom control. Although several types of algicides are commercially available, copper formulations seem to enjoy the greatest popularity due in part to their relatively low toxicity to higher organisms, particularly fish, when applied at accepted algicidal levels (Mackenthun and Cooley, 1952). It is evident from the results of this study that the formation of copper complexes such as copper-citric acid and copper-TEA does slightly inhibit the precipitation of copper from natural waters. However, it is still a matter of debate as to the toxicity of these complexes in their role as algicides. Regardless of this issue, guidelines for the proper proportions of chelated copper formulations are a necessity in water treatment operations involving "on-site" preparations. This study indicates that any greater than a 1:5 (w/w) ratio of either copper sulfate pentahydrate:citric acid monohydrate or copper sulfate pentahydrate: triethanolamine results in little or no additional inhibition of copper precipitation. This study points to the need to carry out field scale investigations to determine the efficacy of using citric acid as a chelant within an economically and ecologically reasonable range (1:0.5 to 1:3) of copper sulfate pentahydrate to chelant ratios.

17. Document Analysis a. Descriptors
Algal Bloom; Algicides; Lakes; Illinois; Algae

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